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Geochemical Investigation of Source of Saline Groundwater at Springs Associated with *Puccinellia howellii* Habitat, Whiskeytown National Recreation Area, Shasta County, California

Natural Resource Technical Report NPS/NRPC/WRD/NRTR—2007/375

ON THE COVER
Puccinellia howellii at Salt Springs at Crystal Creek, Whiskeytown National Recreation Area
Photograph courtesy of Whiskeytown National Recreation Area

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Executive Summary

The Salt Springs at Crystal Creek occupy an approximately one acre area in northern California known to support the only population of *Puccinellia howellii* (Howell's alkali grass) in the world. A California Department of Transportation (Caltrans) highway realignment project in 1991 significantly reduced the spring habitat, and affected the surface flow and distribution of water from the springs. The source of the groundwater emanating from the springs and factors creating the unusual chemistry of the water has previously been unknown. Whiskeytown National Recreation Area requested an investigation of the potential source(s) of groundwater at the site so that they might better manage the site by minimizing potential impacts to the quantity and quality of groundwater discharging from the springs.

Salinity of water at the site ranges from 15 to 35 dS/m (decisiemens/meter, equivalent to mmho/cm), approximately half that of seawater. Although initially extremely alkaline with a pH of 9 to 9.6, the water acidifies and the pH subsequently drops to 5 or 6 as it flows across the site. The resulting unique environment permits *P. howellii* to exist, while at the same time maintaining harsh enough conditions to exclude other plants.

Discharge and temperature measurements, tritium analyses, and stable isotope analyses conducted by Caltrans were used during this analysis. This NPS investigation also relied heavily upon chemical and isotope data from a U.S. Geological Survey (USGS) website which serves as the repository for water chemistry data for hot springs. These data were primarily accumulated by two USGS investigators (I. Barnes and R. Mariner) over a time period of about 40 years (see http://hotspringchem.wr.usgs.gov/info.php).

Tritium analyses performed for samples collected by Caltrans indicate that water emerging at the Salt Springs at Crystal Creek entered the groundwater system as recharge sometime prior to 1953. Most Barnes and Mariner data for springs in Shasta, Tehama, and Trinity Counties plots in a cluster in the same general area on a Piper trilinear plot, suggesting similarities in the water chemistry at those springs. The *P. howellii* springs site data, on the other hand, plot in a different area of the Piper plot, near Puget Sound seawater results produced during a separate investigation by Culhane (1993). The specific conductance versus chloride concentration graph indicates that data for the Salt Springs at Crystal Creek plots along a different linear trend than most other springs. This suggests a different relationship between these two parameters as compared with most other springs in the three-county area.

The $\delta^{18}O$ and δD plot indicates that a group of data, including those from the Salt Springs at Crystal Creek, plots predominantly below the meteoric water line. One possible explanation for this oxygen shift is that the water underwent enrichment during a secondary fractionation process (evaporation). An alternate explanation is that the oxygen shift is due to water-rock interactions, perhaps at an accelerated rate due to geothermal alteration.

Three scenarios were developed regarding potential sources of groundwater to the *P. howellii* springs based on the results of the geochemical analyses and the existing geologic and hydrogeologic information. Scenario 1 suggests that groundwater flowing through the Bragdon Formation picks up salts before being impeded by the Spring Creek Thrust Fault and the nearly

impervious Copley Greenstone. Some evidence in support of this includes the fact that the *P. howellii* spring water chemistry data is similar to that of Puget Sound seawater chemistry data on the Piper trilinear plot. However, based on the results of this investigation, Scenario 1 appears to be the least probable explanation. Although it is possible that the groundwater dissolves minerals as it percolates through these marine rocks, the Bragdon Formation has very low permeability where fracturing and jointing are absent.

Scenario 2 suggests that water discharging at the Salt Springs at Crystal Creek has experienced a deep circulation flow path through the Copely Greenstone. This scenario includes the possibility that the thrust fault is acting as a fault-gouge confining unit, creating a regionally confined aquifer system that has been breached by the high angle faults in the vicinity of the springs. This appears to be the most likely explanation for the saline groundwater that emerges at the *P. howellii* springs site. Due to the mineralogy associated with the Copely Greenstone and the Shasta Bally batholith, this scenario likely would need to include a component of geothermal alteration. The oxygen shift in the Salt Springs at Crystal Creek data on the $\delta^{18}O$ and δD plot may indicate such alteration. As the age of the Shasta Bally batholith makes it an unlikely heat-source candidate, some unknown, more recent heat source would seem likely. Several aspects of other data presented in this study also point to Scenario 2 as the most plausible explanation, including the high ammonium concentrations in water from the Salt Springs at Crystal Creek and the high temperature (30ºC) for Salt Springs at Crystal Creek - East.

Scenario 3 suggests that water emerging at the springs initially followed a path of secondary fracture permeability present throughout a large portion of the Spring Creek Thrust Fault. If this is the case, then this water may emerge at the springs as a continuation along this path - aided by fracturing associated with several high angle faults. This theory is supported by those same arguments made in favor of Scenario 1, and it also is able to explain the presence of regionally extensive secondary permeability in the Bragdon Formation. Consequently, this cannot be ruled out as a plausible explanation for the saline groundwater that emerges at the *P. howellii* springs site.

If groundwater flow characterized by long residence times and deep circulation through fractured Copley Greenstone is the correct paradigm (Scenario 2), then that would likely indicate the springs are not very susceptible to effects from anthropogenic development outside the park boundary. However, the moderately deep flow path depicted in Scenario 3 would likely have shorter residence time and shallower circulation compared to Scenario 2. As such, if Scenario 3 is correct, this would suggest that recharge to the Salt Springs at Crystal Creek would be most susceptible to the effects of anthropogenic development near the margins of the Spring Creek Thrust Fault block.

Finally, it is significant that only a few other springs in the three-county area demonstrated chemical characteristics somewhat similar to the Salt Springs at Crystal Creek. Of these, the "Spring at Bridge Gulch" plotted somewhat similarly on the Piper trilinear diagram, the specific conductance versus chloride concentration graph, and the stable isotope data plot. As such, given the limited tolerance of *P. howellii* for unsuitable habitat, if researchers attempt to establish this rare salt grass at another site, the "Spring at Bridge Gulch" site would be a candidate for further investigation.

Acknowledgements

Water chemistry and isotope data obtained from the U.S. Geological Survey Barnes and Mariner project website formed the primary basis of this study (http://hotspringchem.wr.usgs.gov/info.php). The data specific to Shasta, Tehama, and Trinity Counties are attributed to I. Barnes and W. Evans for water samples that were collected in 1979.

Jennifer Gibson and Brian Rasmussen of Whiskeytown National Recreation Area provided assistance and logistical support for this project at the park level. Their interest in preserving the habitat for *Puccinellia howellii* provided the impetus for this investigation. Jenifer Back, Larry Martin, and Pete Penoyer of the National Park Service, Water Resources Division reviewed drafts of this report and provided critical insights regarding this investigation.

Preparation of this report was initiated by Tom Culhane during the waning days of his tenure with the National Park Service. Tom continued working on the report and completed the first few drafts after taking a job with the Washington State Department of Ecology. Peer reviews and the final revision were coordinated by Larry Martin.

Introduction

The Salt Springs at Crystal Creek occupy an area of approximately one acre in northern California and support the only known population of the grass *Puccinellia howellii* (Howell's alkali grass) in the world. The site is located in Shasta County, California, within Whiskeytown National Recreation Area, adjacent to Highway 299, approximately 32 kilometers west of Redding, near the juncture of Crystal Creek Road (Figure 1). This rare plant depends upon the unique, highly alkaline water conditions that exist at the site.

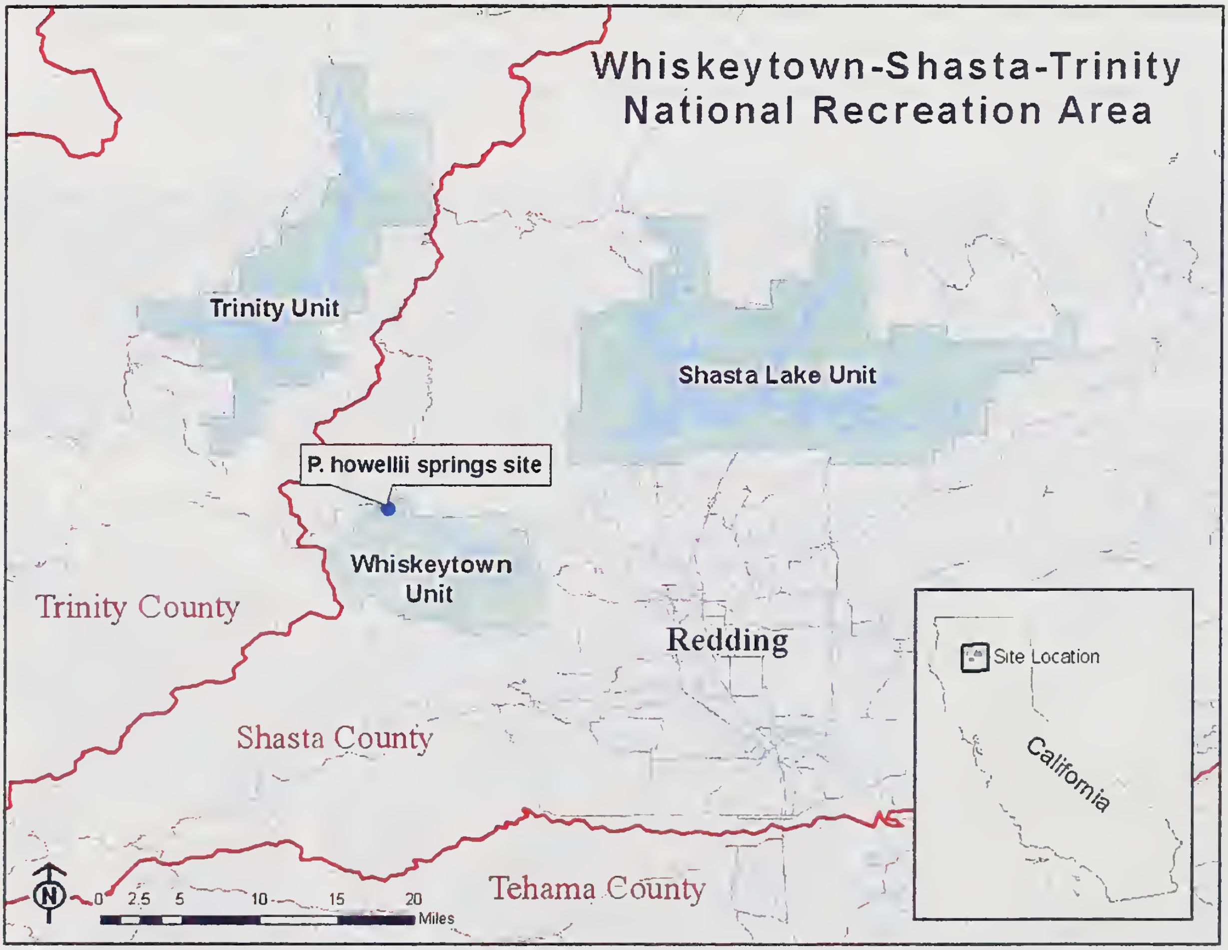

Figure 1. Site location map of *P. howellii* spring study area.

A California Department of Transportation (Caltrans) highway realignment project in 1991 significantly reduced the *P. howellii* habitat. A number of investigations were conducted to assess the potential effect of the highway construction project on the springs. At least one of the studies included theories regarding the source of water for the *P. howelli* springs. However, the primary focus of the Caltrans work was to determine the potential effect of the highway project on the springs, rather than determining the source of water for the springs. Whiskeytown National Recreation Area staff requested that WRD staff conduct an investigation of the potential source(s) of groundwater at the site so that park staff might better manage the site by minimizing potential impacts to the quantity and quality of groundwater discharging from the springs.

Site Description

The *P. howellii* population is unevenly distributed within the complex of mineral springs at an elevation of approximately 1,350 feet along a 1,200-foot reach of Willow Creek. The three main springs are not contiguous on the surface, but likely reflect a contiguous fractured aquifer system in the underlying rock. The individual springs were assigned numbers within the Conservation Agreement for *P. howellii*, entered into by the U.S. Fish and Wildlife Service, the National Park Service, the California Department of Transportation, and the California Department of Fish and Game (National Park Service, 2005). For consistency, that same numbering system is adopted here. Springs 1 and 2 are located west of Crystal Creek Road, with Spring 2 being nearest to Crystal Creek Road (Figure 2). Spring 3 is located to the east of Crystal Creek Road.

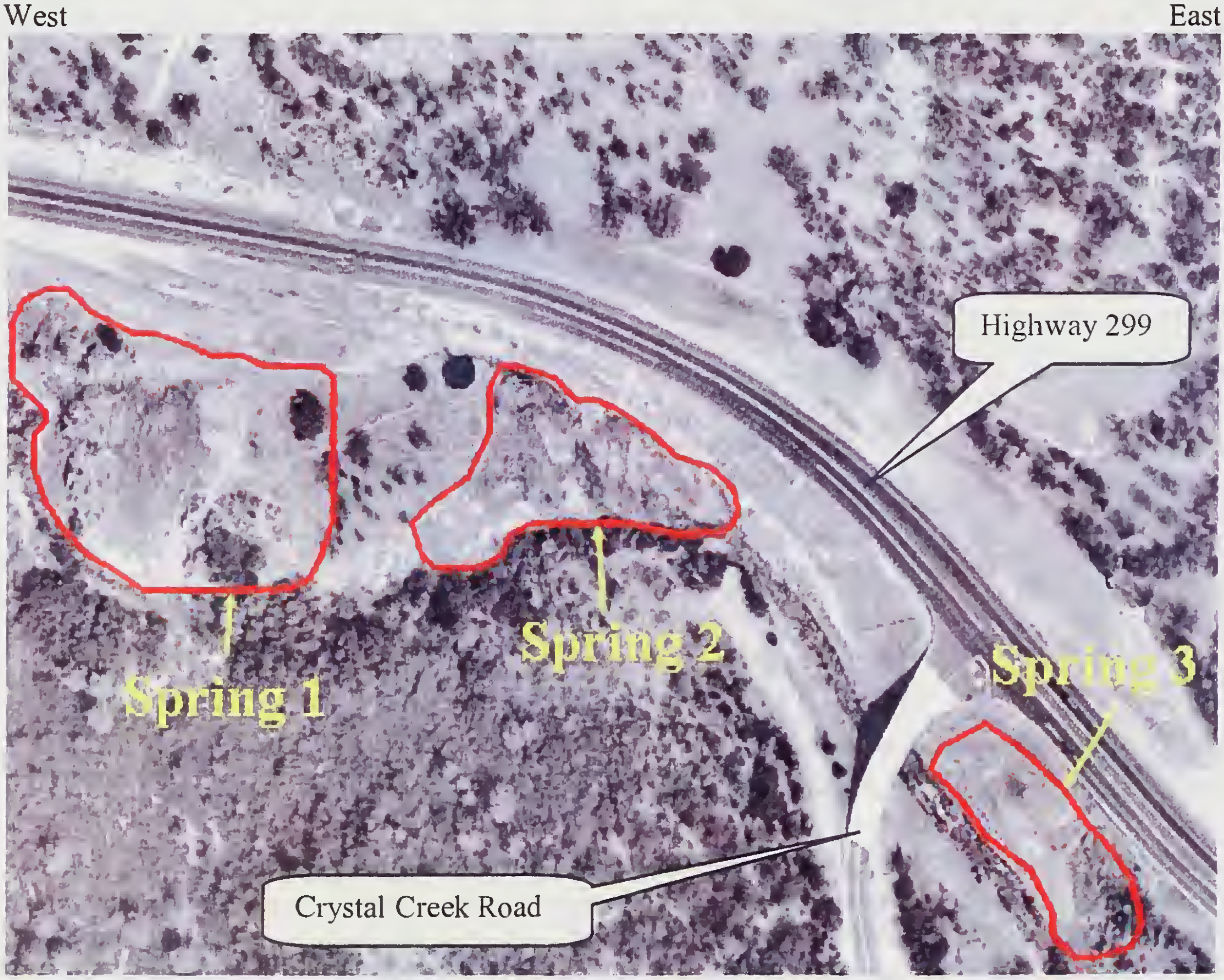

Figure 2. Approximate delineation of Springs 1, 2, and 3.

Sources of Information

Caltrans produced data for temperature, discharge, and water chemistry at five locations (two sites at Spring 1, two sites at Spring 2, and one site at Spring 3). Unpublished results of a Caltrans hydrogeologic site investigation (James, 1990) and information contained in several

other Caltrans memos and draft memos provided useful information and alternative conceptual models for groundwater flow to the springs.

Chemical and isotope data that were obtained from the U.S. Geological Survey (USGS) Barnes and Mariner project website (http://hotspringchem.wr.usgs.gov/info.php) formed the primary basis of this investigation. The data for the *P. howellii* salt springs are referred to as "Salt Spring at Crystal Creek – East" and "Salt Spring at Crystal Creek – West". It is unclear which of the three spring areas at Crystal Creek correspond to the "East" and "West" designation of the Barnes and Mariner data. Identical legal descriptions are provided for both sites. The data for both the "West" and "East" springs are for samples collected July 24, 1979.

During this study, data for a number of other springs in Shasta, Tehama, and Trinity Counties available at the Barnes and Mariner website were also used. The locations of springs in all three counties are indicated in Figure 3 below. Two of the springs plot slightly in Siskiyou County even though the database lists their locations as Shasta County. Data for these springs were included nonetheless, as they were used primarily for context and precise locations were not required.

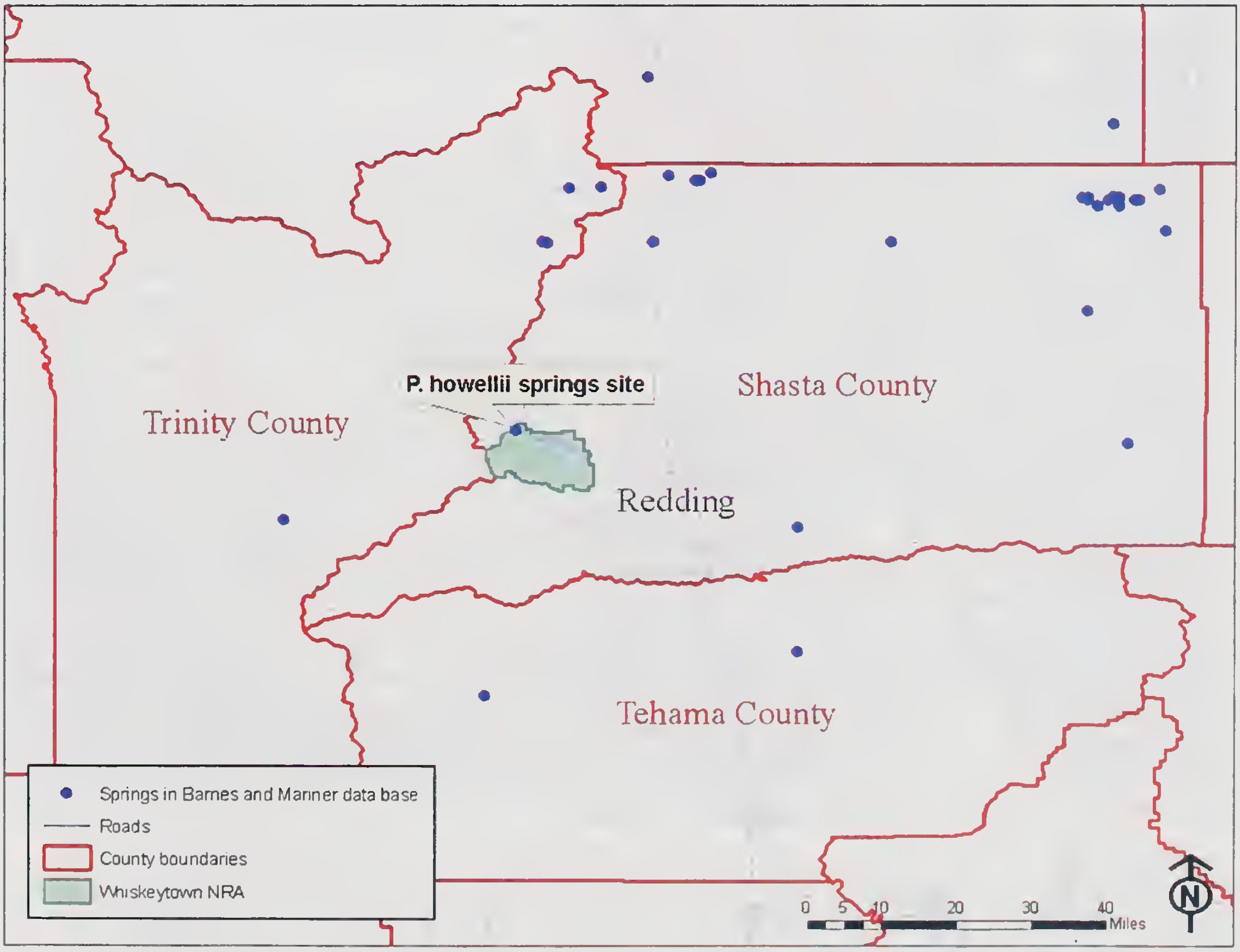

Figure 3. Springs in Shasta, Tehama and Trinity Counties, identified in Barnes and Mariner database.

The primary source of geological information for this study was, "*Geology of the French Gulch Quadrangle, Shasta and Trinity Counties, California*" by Albers (1964). Site specific geologic and hydrogeologic information were available from a 1990 memo entitled, "*Hydrogeology of a Proposed Cut on Highway 299 near Crystal Creek Road by Caltrans*" (James, 1990),and a National Park Service, Water Resources Division trip report by Penoyer and Martin (2007).

Scope of Work
This investigation was based primarily on geochemical analyses and relied entirely on existing data and information. Most of the water chemistry and isotope data are available at the USGS Barnes and Mariner database website. Additionally, some data and reports produced by Caltrans were used during the study. A brief site visit was made on January 14, 2007; however, no other field work was conducted. By integrating the results of the geochemical analyses with existing geologic and hydrogeologic information, several hypotheses regarding potential sources of groundwater and groundwater flow paths to the *P. howellii* springs were developed. However, as this study had a limited scope, it should not be viewed as a comprehensive investigation.

Physical Conditions

Geology
A description of the area's geology is contained in "Geology of the French Gulch Quadrangle, Shasta and Trinity Counties, California" (Albers, 1964). That report indicates that rocks in the area range in age from pre-Silurian (and possibly Precambrian) to Recent. The oldest rocks are the coarsely crystalline Salmon hornblende schist and Abrams mica-schist exposed about 12 miles southwest of the spring. Two probably much younger formations, Copley Greenstone and Balaklala rhyolite, overlie these schists.

The Copley Greenstone of possible Devonian age consists mostly of intermediate and mafic volcanic rocks that crop out at the spring site. This rock is exposed in an area of about one square mile to the west and also over a large area primarily to the southeast. The Devonian Balaklala rhyolite, which is composed of siliceous felsic volcanic rocks, overlies and intertongues with the Copley Greenstone. Overlying the Balaklala in places are beds of dark, siliceous, cherty shale of the Kennett Formation; however, this unit is absent in the vicinity of the springs.

The Copley Greenstone, and in places the Kennett Formation, are overlain by the Mississippian-age Bragdon Formation. The lower part of this formation is composed mainly of shale and siltstone, while the upper part includes coarse grit and conglomerate along with shale and siltstone. Albers reports finding no fossils in the Bragdon Formation in either the French Gulch quadrangle or the adjoining Shasta copper-zinc district. However, Albers does report that about 12 miles to the northeast Diller (1906) reported finding limestone fragments which commonly contained corals and other fossils derived from the Kennett Formation. The Bragdon Formation generally overlies the Balaklala to the north; however, the Spring Creek Thrust Fault has juxtaposed Bragdon Formation directly against Copley Greenstone near the Salt Springs site. The thrust fault contact is visible on the hillside above the highway northeast from Spring 3, where a historic pipeline discharges water to a ditch about 25 feet above the road. Penoyer and

Martin (2007) indicate that both units are highly fractured and jointed in the vicinity of the site, and the Bragdon Formation is somewhat contorted in its lower 3 feet at the contact with the Copley Greenstone.

The Shasta Bally batholith and the Mule Mountain stock are two large plutons occupying an area of more than 100 square miles several miles to the southwest and southeast, respectively. The Mule Mountain stock consists of trondhjemite and albite granite. The Shasta Bally batholith consists mostly of quartz diorite, but locally grades to granodiorite.

Figure 4 is a generalized surficial geology map of the Whiskeytown NRA vicinity, adapted from GIS coverages of NPS Klamath Network area lithology. The map and GIS coverages were developed by the USGS to provide information for the Interior Columbia Basin Ecosystem Management Project. Files are available at: http://science.nature.nps.gov/nrdata/datastore.cfm?ID=37499.

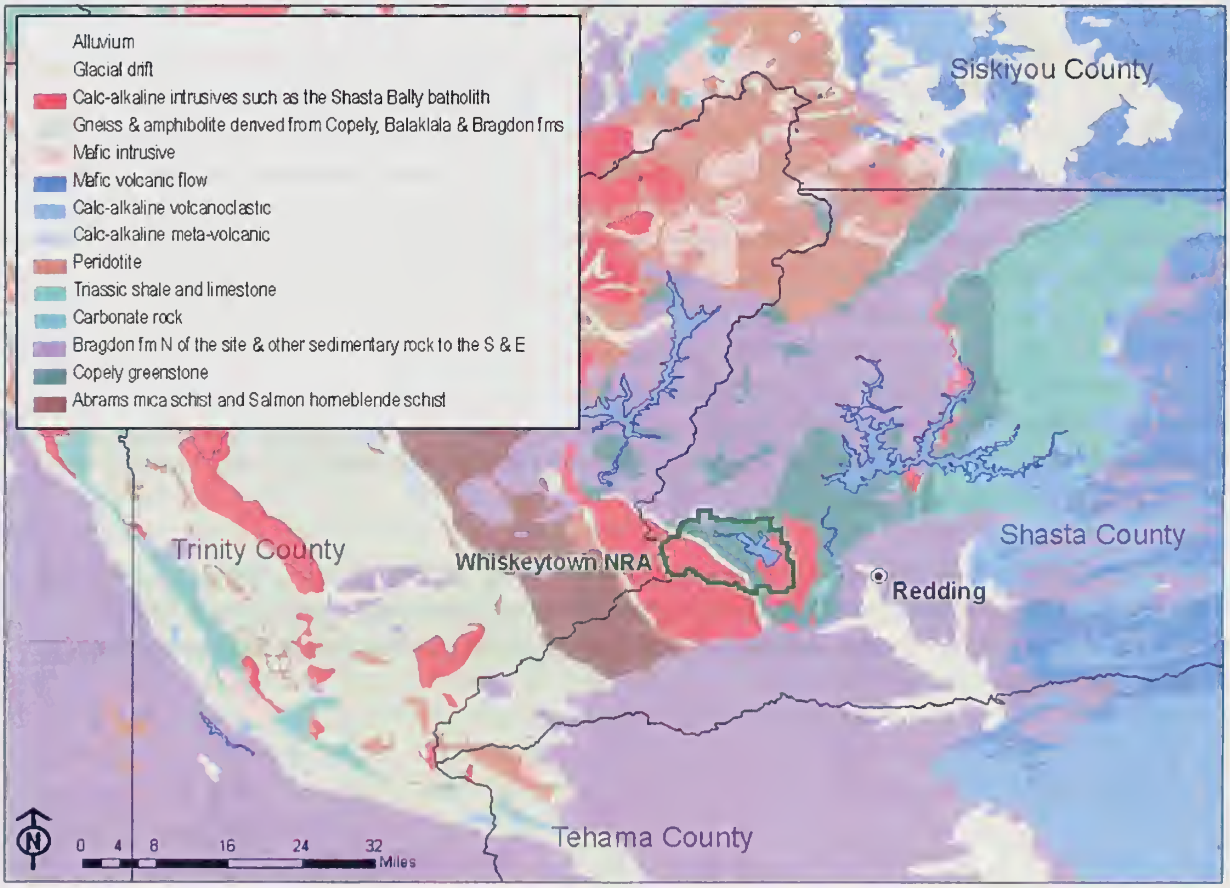

Figure 4. Generalized geologic map of Whiskeytown NRA vicinity (adapted from USGS data).

It may be significant regarding the source of the salinity in groundwater at the site that a number of local rocks were deposited in a marine environment. Kinkel et al. (1956) indicate that two of the oldest rocks in the area, the Salmon hornblende schist and the Abrams mica-schist, contain a large amount of sedimentary material that likely was deposited in oceanic basins. The thrust fault at the Salt Springs site has juxtaposed Bragdon Formation directly against Copley Greenstone, and approximately 12 miles northeast of the site. Diller (1906) reported finding limestone

fragments within the Bragdon Formation, which commonly contained corals and other fossils derived from the Kennett Formation. Additionally, Kinkel et al. (1956) state that sedimentation as recent as the Eocene and Pliocene probably occurred partly in oceanic bays and partly in fresh water.

Although the geologic map on Plate 1 of the Albers report depicts the Spring Creek Thrust Fault as the general boundary between Copely Greenstone and Bragdon Formation in the area, the offset of this fault is unknown. If the Copely Greenstone is Devonian in age (approximately 417 to 354 million years before present (mybp)) and the Bragdon Formation is Mississippian in age (approximately 354 to 323 mybp), the latter unit could have been deposited over the former during a normal deposition sequence.

One source of site specific geologic information is a Caltrans memo by James (1990). That report indicates that the Caltrans data somewhat contradicts the Albers' map, which shows the Spring Creek Thrust Fault located closer to the highway then observed.

In addition to the Spring Creek Thrust Fault, several high angle normal faults, such as the Hoadley Fault, are found in the area. Figure 5 depicts these faults as mapped by Albers. Fault A passes just to the north of the Spring Creek Thrust Fault and the spring site. Penoyer and Martin (2007) question Albers' placement of this high angle fault and note that it would be difficult to trace within the joints and fractures found in the Copely Greenstone. Penoyer and Martin also noted the difficulty in recognizing faults with the extensive soil and vegetative cover that characterize the area and the difficulty in recognizing offsets in relatively homogenous greenstones. For those reasons they suggested that Fault B may actually cross the Spring Creek Thrust Fault and pass through a slice of the Copely Greenstone south of the thrust fault. Both Faults A and B were mapped by Albers as having their downthrown sides on the east. Conversely, Albers indicates the short, high angle fault labeled "C" in Figure 5 as having a throw reversed from that of faults A and B. Fault C occurs just south of the Spring Creek Thrust Fault in the Copely Greenstone.

Although the Albers map provides considerable information regarding the complexity of the site, the work presented in the Caltrans memo by James (1990) and the site survey conducted by Penoyer and Martin (2007), make it clear that the geology of the area is much more complicated than previously mapped.

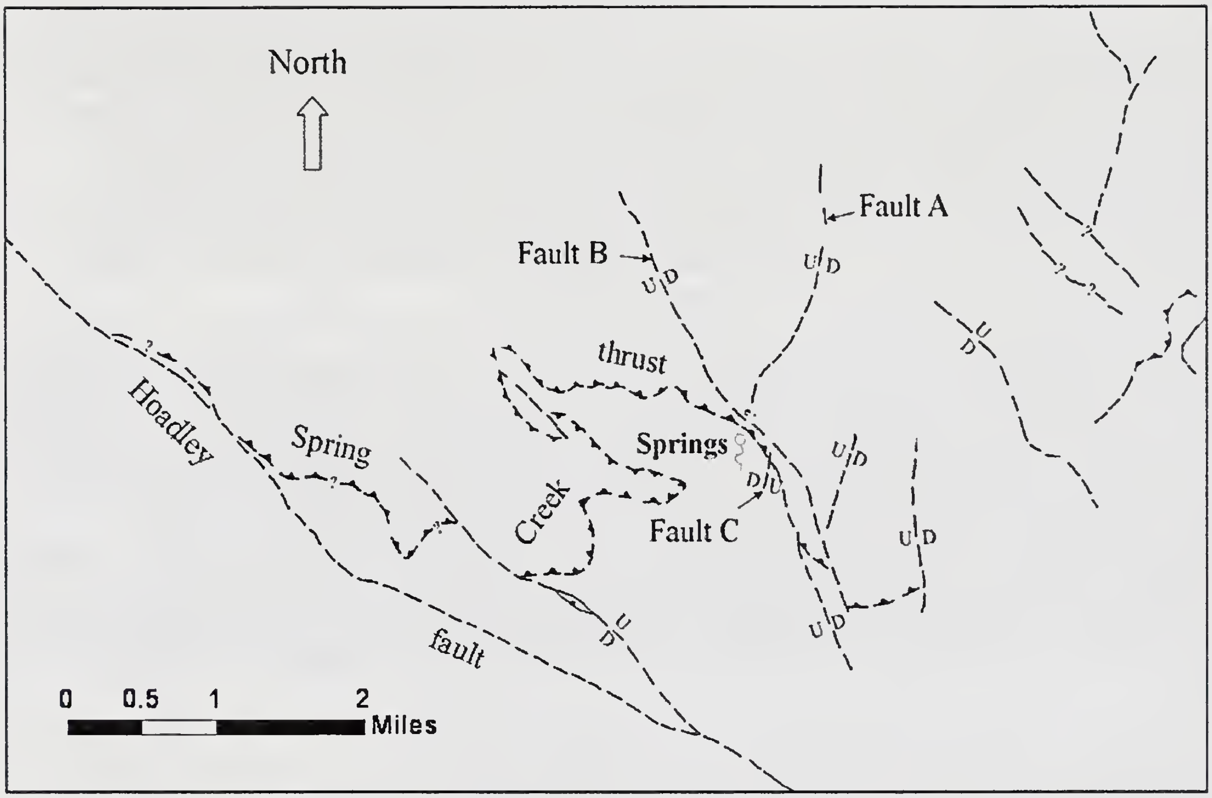

Figure 5. Faults mapped by Albers (1964) in the vicinity of the *P. howellii* springs.

Hydrogeology

Site specific hydrogeologic information is contained in the Caltrans memo by James (1990). The main purpose of that investigation was to determine whether the proposed road cut on Highway 299 near Crystal Creek Road would intercept mineralized water at the *P. howellii* springs in quantities that would significantly alter groundwater flow to the seepage areas.

The Caltrans report theorizes that groundwater flowing through the Bragdon marine-deposited shales and sandstones dissolves salt from the bedrock before being impeded by faults and the nearly impervious Copley Greenstone. The report goes on to suggest the existence of a groundwater flow path within the Copley fracture system allows the water to reach the surface in the vicinity of the springs. A sketch in that report depicts a conceptualization of groundwater flow toward the site. This conceptual model of groundwater flow is essentially the same as Scenario 1 shown in Figure 10 of this report.

More recently, Scott Lewis (pers. comm.), a geologist with Caltrans, has proposed two alternative conceptual models for groundwater flow to the springs. One theory has recharge water entering the Copely Greenstone southwest of the site and northeast of the Shasta Bally batholith, then moving down-gradient to the northeast, where it encounters joints just prior to reaching the Spring Creek Thrust Fault. This conceptual model includes an unspecified heat source beneath the Copely Greenstone, presumably capable of altering the geochemistry of the water.

Lewis' second theory is very similar, with the exception of there being no mixing of recharge water from the surface. Instead, the water comes from a greater depth, from the partial melting of a subducting plate of the earth's crust that would be rich in seawater, resulting in the release of the seawater which then finds its way to the surface via joints and fractures. Lewis' two theories could be evaluated by testing the water at the springs for rare earth elements. If chemical analyses showed rare earth chemistry characteristic of mantle petrology or the influence of seawater, then the second theory (partial melting of a subducting plate) would be more likely. If the analyses did not show a correlation to mantle petrology or seawater, then the first theory (mixing of surface recharge) would be the more likely theory.

According to James (1990), a master fracture system in the Copely Greenstone strikes N 40 to 60 degrees W and dips from vertical to 80 degrees S or 86 degrees N. These joints are oriented sub-parallel to the regional structural trend of the Spring Creek Thrust Fault, Hoadley Fault, fold axes in the Bragdon Formation, and the general contact between the Shasta Bally Batholith and the Copley Greenstone. This fracture system was well exposed in the highway cut during construction, and quartz veins up to 14 inches thick were found in some fractures. James (1990) states that secondary fractures probably allow groundwater to escape confinement of the master fracture/quartz vein system. The report also states that rock cores taken in the area indicated that the Copley Greenstone is massive and non-porous with a few, tight, planar and non-planar fractures.

A significant portion of this Caltrans report was dedicated to defining mineralized water for the purposes of the investigation and then providing a map of mineralized and non-mineralized water areas. The report states that the scattered locations of mineralized seeps in the project area result from the orientation of fractures in the bedrock and from the piezometric surface. The report goes on to state that:

> Although seepage areas 1 and 2 (see Figure 2) contain 50 and 25 feet of vertical relief, individual seeps in the upper portions of the areas often produce more water than lower seeps. Therefore, the open and/or interconnecting nature of the fractures contributes more toward the productivity of seeps than does the piezometric surface.
>
> Map 2 shows the distribution of seeps, etc. No mineralized seeps occur in the Mississippian age Bragdon Formation. Within the Devonian age Copley Greenstone, the distribution of mineralized seeps generally occurs within an elongated belt that parallels the master fracture system between the highway and Willow Creek, The master fracture system with its associated quartz veins probably greatly restricts the direction in which groundwater can move. Although most seeps are obscured by highway fill or thin rocky soil, some seeps issue from bedrock along master fractures or where the master fracture system is cross-cut by secondary fractures.
>
> All of the seeps in seepage areas 1 and 2 contain mineralized water. Some also contain combustible gas and others a distinct H_2S smell. Translucent white salt deposits coat the soil and rocks scattered throughout the area. Most of the seeps occur along the northeast side of Willow Creek on both sides of the existing highway, but three mineralized seeps occur on the southwest side of Willow Creek.

> The three mineralized seeps on the southwest side of Willow Creek occur about 220 to 300' downstream from the Crystal Creek Road Bridge and lie along a trend from the proposed cut that is consistent with the strike of the master fracture system. If the source of the mineralized water in these seeps is the same as that for the seeps near the cut, then excavations such as the existing highway cut or stream channel erosion (down cutting) have not disrupted groundwater movement to the seeps.

It is important to note that the USGS wrote a response to this Caltrans hydrogeologic report, and Caltrans responded with a memo on April 15, 1991. Judging by the tone of the Caltrans response, the USGS questioned some of the Caltrans interpretations. Beyond functioning as a response, this Caltrans memo reports other work that provides evidence for both mineralized and non-mineralized sources for the springs. Such evidence apparently included analyses of water from four borings that produced water of two chemical types, possibly separated by groundwater barrier(s) such as a fault plane. Water entering one borehole completed south of the Spring Creek Thrust Fault within the Copely Formation produced water at a depth between 41 to 47 feet that was only slightly mineralized, suggesting that meteoric water may occur at significant depth. This borehole is approximately 100 feet north of Hwy. 299, north of Spring 1.

Based on all the available evidence, it is clear that in an unaltered state the Copely Greenstone and the well-indurated Bragdon Formation are incapable of transmitting significant amounts of water. However, a high degree of fracturing and jointing evident in outcrops in the area indicate the presence of considerable secondary permeability. Furthermore, the Spring Creek Thrust Fault and several high-angle normal faults converge near the springs. The fracturing and jointing in the rocks likely are a result of this faulting, and additionally, the faults themselves can act as conduits or barriers. Due to the intersection of the faults near the springs, it is likely that at least some of the faults act as conduits that carry water from some depth up to the surface. However, faults can also act as barriers. Consequently, it is possible that water traveling through conduits created by the high angle faults may encounter a barrier in the form of the Spring Creek Thrust Fault, for example, and that may force water to the surface.

In addition to the tectonic factors regarding the occurrence of the *P. howellii* springs, topography has played a significant role. Groundwater movement requires an elevation change in order to drive it. Groundwater discharging at Salt Springs at Crystal Creek entered the aquifer as recharge at some up-gradient location, and in the case of the *P. howellii* site, it is significant that the springs occur at a topographic low in a major stream drainage between two mountainous areas. If conduits exist through the rock, then groundwater recharging either to the north or south would have the head differential necessary to flow down-gradient toward the springs.

Water Temperature

Water temperature data are available from both the Caltrans work and the Barnes and Mariner database; however, data from these sources are somewhat contradictory. Some temperature data are provided in a Caltrans draft memo by Casey (1994) entitled, "Mineral Spring Hydrology Monitoring Study." Table 5 in that report includes about 278 temperature measurements for sites 1A, 1B, 2A, 2B and 3 collected between May 23, 1992, and December 29, 1993. Unfortunately, the accuracy of these data is questionable. A visual inspection suggests these data generally fall

between 19 to 23 degrees C, and they range from a low of 8 degrees to a high of 29 degrees. However, these latter values are outliers. More importantly, there is a relationship between air temperature and the recorded water temperatures, and the report states:

> The temperature of the spring water may be dramatically affected by the monitoring method. As the water runs over the rocky terrain, the temperature of the spring water is influenced by air and ground temperatures. On days with extreme temperatures, the measured temperature of the water exiting the pool will be different than the actual temperature of the water exiting the spring.

This indicates that there may be a QA/QC problem with the data and further calls into question other temperature data collected by Caltrans. For example, a draft memo by Caltrans (January 21, 1993) titled "Preliminary analyses of construction activity and earthquakes effects on some physical and chemical aspects of mineralized seeps at Crystal Creek, California" contains some temperature information. That document states:

> Seeps 1A, 1B, and 3A flow a short distance from the source to a measuring point, and they show water temperatures at the site range from 12 to 15 degrees centigrade regardless of air temperatures ranging from 3 to 24 degrees on these dates.

The phrase "a short distance from the source to a measuring point" indicates the water would have cooled prior to measurement, and thus these are not indicative of water emerging at the spring orifice.

In contrast to the Caltrans data, information in the Barnes and Mariner database indicates water temperatures of 19 and 30 degrees C (66 and 86 degrees F) for Salt Spring at Crystal Creek "West" and "East", respectively. The data for the "East" spring is significantly warmer then those reported by Caltrans (with the exception of one unreliable outlier). The important question is whether this 30 degrees C value can be believed. If so, this has significant ramifications for the interpretation of the spring site, as such a warm temperature either suggests the water has undergone a deep flow path and/or has encountered a geothermal heat source along the way. Additionally, this raises the question of whether water from the "East" spring could potentially have been hotter in 1979, when I. Barnes and W. Evans visited the site, than it is today.

Discharge

James (1990) indicates that the seeps at the *P. howellii* site collectively produce about 18.9 gpm. However, there is no information provided as to how this estimate was derived. More detailed information is provided in an April 1992 Caltrans memo entitled, "Flow monitoring for Crystal Creek Curve realignment on Route 299 in Shasta County". These data were gathered in order to evaluate whether blasting associated with the highway alignment affected spring flow. Those data are provided in Table 1 and graphed in Figure 6 below. However, it is clear that due to the challenges of measuring diffuse discharge, these data represent only a fraction of flow at the site.

Table 1. Caltrans *P. howellii* springs discharge data in milliliters/second.
(10 ml/s = .16 gpm, or 1gpm = 63 ml/s)

Date	Spring 1A	Spring 1B	Spring 2A	Spring 2B	Spring 3A
2/8/91	55.80	12.40	19.10	32.80	32.40
2/16/91	56.80	13.00	18.10	31.50	32.40
3/9/91	57.00	13.60	22.50	39.60	35.20
3/15/91	54.70	12.80	21.80	36.80	34.00
3/21/91	55.90	13.70	50.30	86.20	64.30
3/27/91	55.60	13.00	34.10	71.70	41.00
3/28/91	56.30	13.30	27.10	56.00	40.00
4/1/91	56.10	13.70	22.60	37.00	34.30
4/2/91	57.10	13.40	23.00	34.10	34.70
4/4/91	56.40	13.40	21.70	32.00	33.60
4/5/91	61.50	15.30	22.40	41.20	36.00
4/9/91	56.69	13.83	16.71	31.55	32.31
4/11/91	56.24	13.50	17.67	29.85	33.00
4/17/91	57.34	13.63	17.68	32.26	33.10
4/19/91	56.50	13.56	16.41	30.31	33.73
4/29/91	56.05	13.55	18.92	29.99	32.05
5/3/91	56.82	13.66	19.67	30.86	32.84
5/6/91	55.68	13.49	19.07	31.45	32.36
5/23/91	56.95	13.42	14.00	31.30	31.85
5/28/91	56.37	14.05	18.48	31.65	32.31
6/7/91	55.62	13.72	18.67	30.58	32.05
6/17/91	54.64	13.50	16.37	30.44	32.15
7/10/91	52.36	14.08	18.10	30.26	31.90
8/19/91	50.92	15.70	22.50	32.73	34.45
9/12/91	48.69	14.67	22.68	33.56	36.99
10/1/91	44.76	14.91	22.78	32.36	39.84
10/17/91	43.82	15.81	21.19	33.36	36.30
11/4/91	42.05	14.71	17.62	33.84	34.25
11/21/91	43.03	14.28	18.50	32.89	37.81
2/7/92	57.08	12.64	20.62	32.57	52.63
3/3/92	57.14	14.35	22.15	37.88	39.29
3/16/92	57.80	16.27	27.62	69.93	44.15
3/19/92	56.56	15.23	27.28	52.49	40.16
3/25/92	56.88	15.57	22.27	37.30	39.76
3/26/92	59.59	18.08	21.90	36.29	38.46
3/26/92	57.27	16.61	21.95	36.29	39.44
3/27/92	58.34	16.94	22.02	35.27	38.53
3/27/92	58.13	16.72	21.97	33.27	38.83
3/28/92	58.89	16.69	21.27	38.16	37.80
3/28/92	56.94	16.63	21.34	32.89	37.03
3/28/92	58.07	16.61	21.27	33.78	37.87
3/29/92	58.89	16.66	21.25	33.27	37.66
3/29/92	58.20	16.90	21.05	34.30	37.17
3/29/92	57.40	16.84	21.32	34.01	37.87
3/30/92	59.10	16.58	22.53	36.17	36.63

3/31/92	57.34	16.50	21.37	32.47	36.10
4/1/92	58.10	16.85	21.18	31.97	36.90
4/2/92	56.56	16.60	21.67	31.69	36.63
4/3/92	57.21	16.72	21.93	34.31	37.95
4/4/92	55.99	16.63	21.83	32.63	36.04
4/4/92	56.82	16.99	22.05	32.41	36.76
4/5/92	63.13	15.96	21.07	30.91	35.52
4/5/92	56.95	16.65	21.37	31.10	35.97

Figure 6 indicates somewhat consistent flow, but also with some variability. The more constant aspects of the data seem indicative of a regional groundwater flow system, while the variable portions are consistent with a more local source. Similar conclusions have been made by previous researchers such as Cooper et al. (2006). More detailed analyses of the flow data are impossible due to compromises associated with the measurement of diffuse flow at the site.

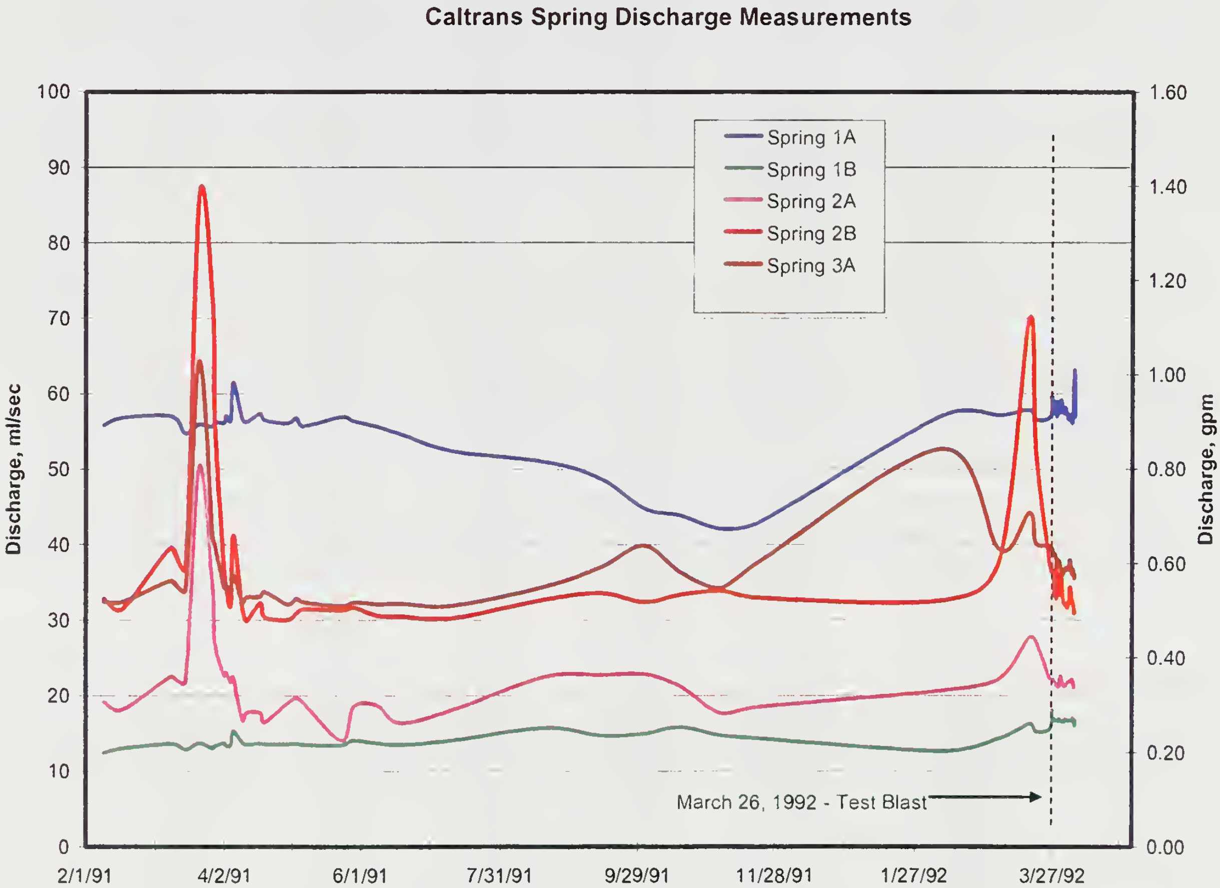

Figure 6. Caltrans discharge data at the spring site, February 8, 1991 through April 5, 1992.

Water Chemistry

Salinity at the site ranges from 15 to 35 dS/m (dS/m is equivalent to mmho/cm), approximately half that of seawater (Levine et al., 2002). Although initially extremely alkaline with a pH of 9 to 9.6, the water becomes acidic as it flows as sheet flow across the site. This acidification is likely due to the oxidation of hydrogen sulfide to sulfuric acid as the water flows over the gravel substrate and interacts with decomposing organic matter (Cooper and Wolf, 2006). The pH subsequently drops to 5 or 6. An alternative hypothesis for the pH decrease is that it is the result of equilibration of the water to normal atmospheric concentrations of carbonate-bicarbonate after precipitation of carbonate at the spring orifices.

P. howellii does not grow near the highly alkaline discharge points, but thrives below the springs where the water has been acidified. Discharge volume and chemistry remain fairly stable year-round (Casey, 1994; CH2M Hill 1991-1992). The resulting unique environment permits *P. howellii* to exist, while at the same time maintaining harsh enough conditions to exclude other plants at the site.

Tritium Dating

A memo from the USGS (Coplen, 1992) reports results of oxygen isotope and tritium analyses performed for samples taken by Caltrans from five locations early in 1992. The results of those analyses are as follows:

Table 2. Caltrans oxygen isotope and tritium analyses performed in early 1992.

Site Designation	Tritium content	$\delta^{18}O_{VSMOW}$
Crystal Creek 1A	0.3 $\pm$ 0.3 TU	-7.00%
Crystal Creek 1B	0.3 $\pm$ 0.3 TU	-6.65%
Crystal Creek 2A	0.6 $\pm$ 0.3 TU	-6.20%
Crystal Creek 2B	0.9 $\pm$ 0.3 TU	-6.15%
Crystal Creek 3A	0.6 $\pm$ 0.3 TU	1.40%

Beginning in 1953 large quantities of man-made tritium (^3H) entered the hydrologic cycle as a result of large-scale atmospheric testing of thermonuclear bombs. It has been estimated that the natural tritium concentrations of precipitation prior to testing was about 5 to 20 tritium units (TU) (Freeze and Cherry, 1979). Since the half life of tritium is 12.3 years, groundwater recharged prior to 1953 is expected to have tritium concentrations below about 2 to 4 TU. In the case of the sampling conducted by Caltrans, the tritium results ranged from 0.3 to 0.9. This indicates that this water entered the groundwater system as recharge sometime prior to 1953.

Major Dissolved Constituents

Caltrans conducted sampling of water at five locations at the site on 11/4/91, 3/18/92, 4/3/92, 5/1/92, 5/19/92, 8/17/92 and 1/28/99. A number chemical analyses were performed on these samples to help determine whether there were any changes at the site as a result of road realignment activities. Unfortunately those analyses did not include several constituents necessary to construct a Piper trilinear diagram plot. The Barnes and Mariner database contains more complete major dissolved constituent data. Those data are presented in Table 3 below. In

instances where multiple samples were collected from the same source, the results were averaged for that source. In cases where the table indicated uncertainty in a value, the data were accepted as indicated, and when the data indicated that values were below certain detection limits a value of half the detection limit was used. A value of zero was used for the carbonate data, since no data were provided on the Barnes and Mariner website.

Table 3. Barnes and Mariner major dissolved constituent data for springs in Shasta, Tehama, and Trinity Counties and Puget Sound seawater results by Culhane (1993) in mg/l.

Spring Name	Ca	Mg	Na	K	Cl	CO3	HCO3	SO4
Adjumawi Lava Springs	10.9	7.7	15.1	2.7	4	0	113	1.74
Altoona Quicksilver Mine well	28	39	3710	220	1560	0	8060	352
Altoona Spring	51	210	3600	290	1300	0	8310	460
Castle Crag Spring	180	230	1100	31	1100	0	2780	1
Castle Rock Springs	170	190	975	21	950	0	2315	3
Crystal Spring	7.9	4.6	8.8	1.8	2.12	0	72	1.05
Deadshot Springs at Deer Lick Springs Resort	1600	7.6	1300	7.7	3800	0	756	1050
Hunt Hot Spring	52	0.05	300	4.3	140	0	62	520
MacArthur city well	15.8	2.6	22.8	2.5	5.7	0	90	15.2
Pit #1 outflow	10	7	13.5	2.7	3.6	0	97	1.49
Puget Sound seawater	355	1110	9000	341	17600	0	108	2290
Rainbow Spring	8.8	6.7	14.2	2.7	4.6	0	90	1.75
Salt Spring at Crystal Creek - West	1150	0.25	2650	7.7	6100	0	52	0.5
Salt Spring at Crystal Creek-East	2000	0.56	5000	16	11100	0	10	0.5
Shiloah Mineral Springs	4.5	25	325	25	380	0	382	37
Soda spring in Asbestos Gulch	50	200	3400	280	1300	0	8100	440
Spring ~150 ft W. of magadiite vein	1.2	0.2	7550	210	7500	0	6000	132
Spring ~500 yds uphill from magadiite vein	2.3	7.3	1770	32	2270	0	745	4.8
Spring at Bridge Gulch	1000	285	4150	24	9200	0	114	0.5
Spring from serpentine-dacite contact	1.9	0.04	10170	211.5	11890	0	5910	358.5
Spring in vein of magadiite	3.3	0.05	3370	85	3980	0	2200	136
Spring; inside Soda Creek Temple	184	235	1200	40	1140	0	3060	3.8
State Park	10.9	7.7	15.1	2.5	3.8	0	115	1.71
Sulphur Spring on south side of Castle Crag	0.8	2.5	3550	125	2650	0	4850	360
Unnamed cold spring	6.85	9.317	9.883	2.983	5.583	0	89.83	2
Unnamed spring - Heitman Ranch	62	28	14	1.8	0.5	0	295	25
Unnamed spring #1 - Fall River	11.8	7.2	5	1.5	1.1	0	82	1.15
Unnamed spring #2 - Fall River	8.6	5.2	7.2	1.8	2.2	0	63	1.04
Unnamed spring #3 - Fall River	8.4	6	12.1	2.5	4	0	73	1.58
Unnamed spring #4 - Fall River	8.5	6.2	12.5	2.2	4.1	0	83	1.67
Unnamed spring at north end of Big Lake	11.63	8.367	14.2	2.7	3.233	0	110	1.513
Unnamed spring on Ja She Creek	10.5	7.533	14.93	2.833	4.067	0	103.3	1.77

Unnamed spring on Jacobsen Ranch	8.4	5.8	14.5	2.3	4.7	0	82	1.6
Unnamed spring on Lava Cr.	8.7	6.3	13.1	2.5	4.2	0	83	1.54
Unnamed spring on Spring Cr.	8.7	6.3	13.7	2.7	4.5	0	86	1.63

Figure 7 is a Piper trilinear diagram plot of all of the major dissolved constituent data for Shasta, Tehama, and Trinity Counties available in the Barnes and Mariner database. In addition, data for seawater collected from the Puget Sound just off of Whidbey Island, Washington (Culhane, 1993) is plotted.

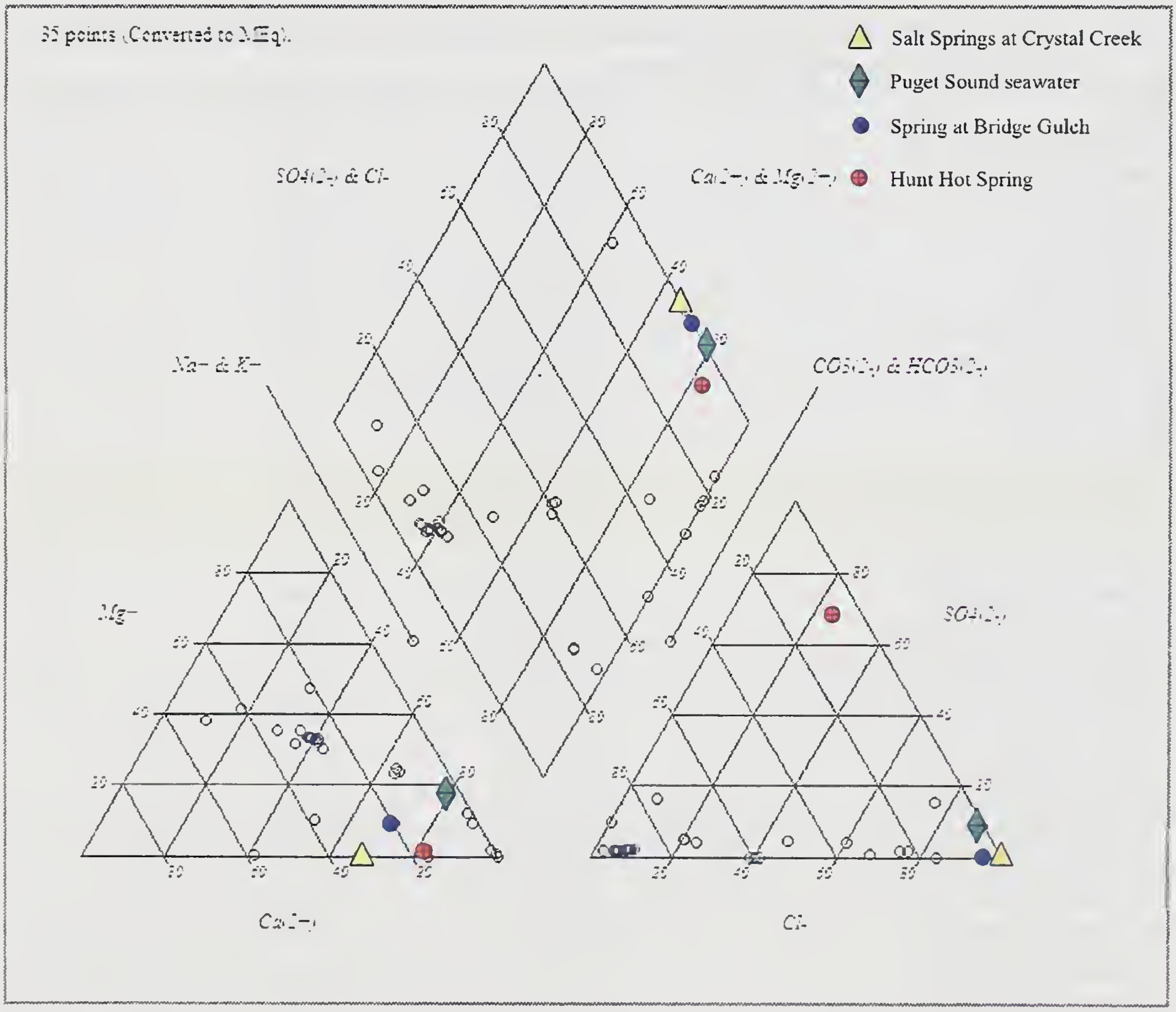

Figure 7. Piper trilinear diagram for Barnes and Mariner data for springs within Shasta, Tehama, and Trinity Counties and Puget Sound seawater results by Culhane (1993).

One obvious observation regarding this plot is that most data for springs in the three-county area plot somewhat linearly in all three sections of the diagram (the diamond and both triangles). This suggests that the water may be evolving along a similar flow path. Conversely, the Salt Springs at Crystal Creek data tend to plot away from these other data and near the Puget Sound seawater results. This suggests not only differing chemistry relative to the other springs, but also

potentially a connection between the water at the *P. howellii* springs and a source of minerals somehow linked to seawater. For reference, Spring at Bridge Gulch and Hunt Hot Spring are also labeled, as they plot in the same vicinity as the data for Salt Springs at Crystal Creek in certain sections of the chart.

In addition to the Piper trilinear diagram plot, the Barnes and Mariner data were also used to analyze the relationship between specific conductance and chloride concentration for springs in Shasta, Tehama, and Trinity Counties. The data used are found in Table 4 and plotted in Figure 8.

Table 4. Barnes and Mariner specific conductance and chloride concentration data for springs in Shasta, Tehama, and Trinity Counties.

Name	Date	Spec. Cond. (mS)	Cl (mg/l)
Adjumawi Lava Springs	7/31/1998	177	4
Castle Crag Spring	8/20/1975	5880	1100
Castle Rock Springs	8/20/1975	5140	950
Crystal Spring	7/31/1997	46	0.24
Crystal Spring	10/22/1998	176	4
Hunt Hot Spring	8/21/1973	1630	140
MacArthur city well	11/6/1997	203	5.7
Pit #1 outflow	10/21/1998	160	3.7
Rainbow Spring	9/5/1997	161	4.6
Salt Spring at Crystal Creek - West	7/24/1979	15900	6100
Salt Spring at Crystal Creek-East	7/24/1979	26700	11100
Shiloah Mineral Springs	8/20/1975	1610	380
Spring at Bridge Gulch	7/26/1979	22600	9200
Spring in vein of magadiite	5/13/1968	13860	3980
Spring; inside Soda Creek Temple	5/14/1968	6700	1140
State Park	6/23/1998	176	3.8
Sulphur Spring on south side of Castle Crag	7/28/1979	13100	2650
Unnamed cold spring	9/4/1974	112	2.8
Unnamed cold spring	8/30/1974	315	23
Unnamed cold spring	9/7/1974	64.7	2.3
Unnamed cold spring	9/6/1974	101	4.2
Unnamed cold spring	8/20/1975	137	0.9
Unnamed cold spring	7/25/1974	150	0.3
Unnamed cold spring	8/14/1980	16	0.5
Unnamed spring #1 - Fall River	7/31/1997	136	1.1
Unnamed spring #2 - Fall River	7/31/1997	113	2.2
Unnamed spring #3 - Fall River	7/31/1997	142	4
Unnamed spring #4 - Fall River	7/31/1997	146	4.1
Unnamed spring at north end of Big Lake	6/23/1998	179	3.1
Unnamed spring at north end of Big Lake	10/22/1998	181	3.3
Unnamed spring on Ja She Creek	6/23/1998	172	4

Unnamed spring on Ja She Creek	7/31/1998	173	4.1
Unnamed spring on Ja She Creek	10/24/1998	174	4.1
Unnamed spring on Jacobsen Ranch	8/1/1998	148	4.7
Unnamed spring on Lava Cr.	11/4/1997	152	4.2
Unnamed spring on Spring Cr.	11/4/1997	157	4.5

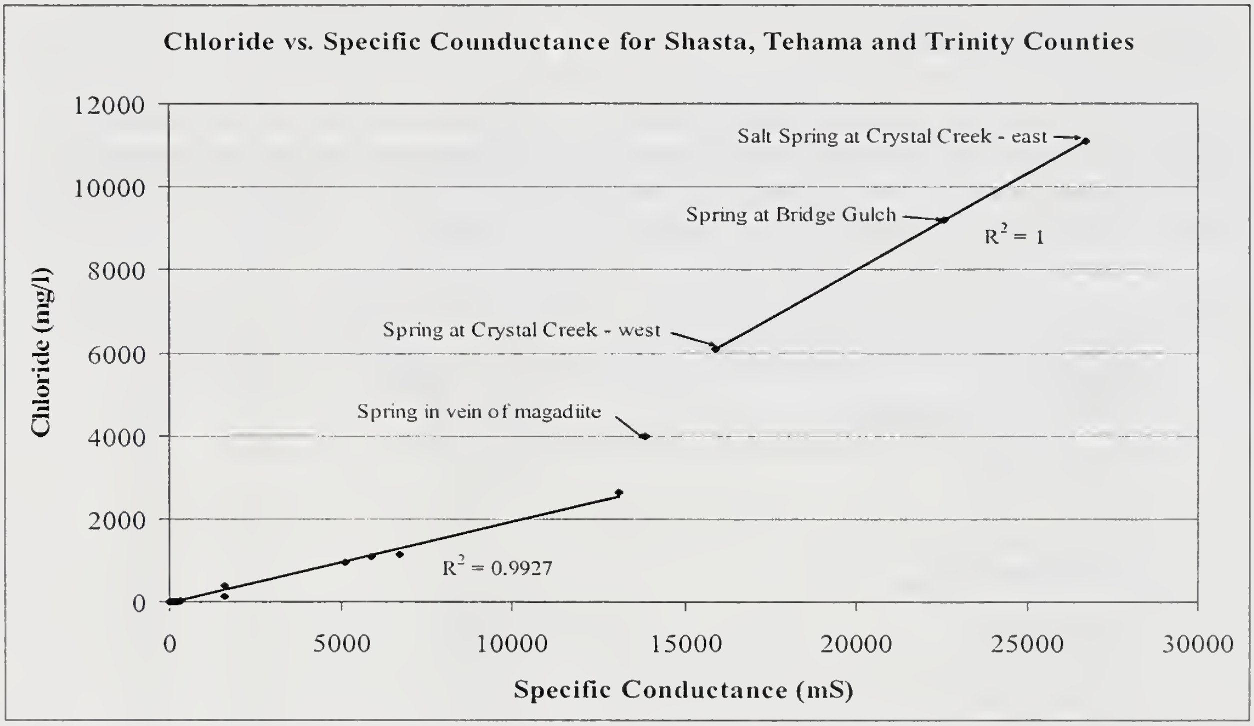

Figure 8. Specific conductance versus chloride concentration for springs in Shasta, Tehama, and Trinity Counties.

Figure 8 suggests the Salt Springs at Crystal Creek data have specific conductance versus chloride concentration relationship that is different from most other springs in the three-county area. Specifically, all but four of the springs plot fairly linearly, with an R^2 coefficient of 0.9927. Conversely data from three of the four remaining springs plot along a significantly different linear trend. Although the conclusions that can be drawn from this graph are limited, the relationships depicted do suggest that the chemistry of water from the four springs is different than that of most other springs in the area.

Stable Isotope Analyses

Most of the world's precipitation originates from the evaporation of seawater. The temperature, altitude, and distance from the ocean affect the hydrogen and oxygen isotope ratios in precipitation. In general, precipitation becomes progressively more depleted (more negative in value) as water vapor condenses and an air mass moves inland from the ocean. Precipitation that occurs further inland and at higher elevations has a lower relative amount of heavier isotopes than precipitation that occurs near the ocean.

The isotopic composition of water is generally reported as delta values (δ), which are reported in units of parts per thousand (permil, ‰) relative to a standard of known composition. The standard often used is Standard Mean Ocean Water (SMOW). The δ values are calculated by:

$$\delta \text{ (in ‰)} = (R_x/R_s - 1)*1000$$

where R denotes the ratio of the heavy to light isotope (e.g., $^{18}O/^{16}O$), and R_x and R_s are the ratios in the sample and standard, respectively. The $\delta^{18}O$ and δD values measured in precipitation from throughout the world are linearly correlated and distributed along a line known as the meteoric water line (Craig, 1961).

Caltrans did not have δD analyses performed on the samples they collected in 1992; thus, it is not possible to plot their data against a meteoric water line. Isotope data from the Barnes and Mariner database are tabulated in Table 5. As before, where multiple samples were collected from the same source, the results were averaged for that source.

Table 5. Barnes and Mariner $\delta^{18}O$ and δD data for springs within Shasta, Tehama, and Trinity Counties.

Spring Name	Date Collected	$\delta^{18}O$	δD
Adjumawi Lava Springs	7/31/1998	-13.3	-100.0
Altoona Spring	7/27/1979	-1.8	-59.0
Big (?) Spring	9/13/1993	-13.2	-97.0
Castle Crag Spring	8/20/1975	-10.6	-82.0
Castle Rock Springs	8/20/1975	-10.6	-80.0
Crystal Spring	8/25/1987	-13.5	-98.6
Deadshot Springs at Deer Lick Springs Resort	7/26/1979	-10.9	-81.0
Eastman Spring	12/31/1969	-13.5	-102.0
Hunt Hot Spring	8/21/1973	-13.3	-94.0
MacArthur city well	11/6/1997	-13.5	-100.0
Pit #1 outflow	8/4/1998	-13.3	-96.7
Rainbow Spring	9/5/1997	-13.6	-101.0
Rising River	9/13/1993	-13.9	-101.0
Salt Spring at Crystal Creek - West	7/24/1979	-6.6	-64.0
Salt Spring at Crystal Creek-East	7/24/1979	-3.2	-52.0
Shiloah Mineral Springs	8/20/1975	-10.8	-77.0
Spring at Bridge Gulch	7/26/1979	-8.5	-77.0
State Park	6/23/1998	-13.3	-99.0
Sulphur Spring on south side of Castle Crag	7/28/1979	-4.2	-65.0
Tuscan Spring #1	6/25/1990	5.6	-15.0
Tuscan Spring #2	6/25/1990	6.0	-16.0
Tuscan Spring #3	6/25/1990	5.8	-15.0
Unnamed cold spring	5/15/1974	-10.4	-71.4
Unnamed spring #1 - Fall River	7/31/1997	-13.2	-94.0

Unnamed spring #2 - Fall River	7/31/1997	-13.6	-99.0
Unnamed spring #3 - Fall River	7/31/1997	-13.7	-101.0
Unnamed spring #4 - Fall River	7/31/1997	-13.7	-101.0
Unnamed spring at north end of Big Lake	6/23/1998	-13.3	-98.8
Unnamed spring on Ja She Creek	6/23/1998	-13.5	-100.5
Unnamed spring on Jacobsen Ranch	8/1/1998	-13.6	-100.0
Unnamed spring on Lava Cr.	7/14/1994	-13.6	-101.0
Unnamed spring on Spring Cr.	11/4/1997	-13.8	-101.0

The data for "Salt Spring at Crystal Creek – West" probably corresponds with the Spring 1 location as designated in this report (Figure 2). There is also good agreement between the $\delta^{18}O$ results for that spring (-6.6%) and the Caltrans results for Spring 1A and 1B (-7.00% or -6.65%, listed previously). Caltrans reported $\delta^{18}O$ results of -6.2, -6.15 and +1.4% for springs 2A, 2B and 3B, respectively, while the result for the "Salt Spring at Crystal Creek – East" spring was -3.2%. This lack of a match may be partially due to the mixing of groundwater. Nonetheless the absence of agreement for the $\delta^{18}O$ results creates uncertainty regarding the veracity of the data.

The Barnes and Mariner data plot relative to the meteoric water line as shown in Figure 9.

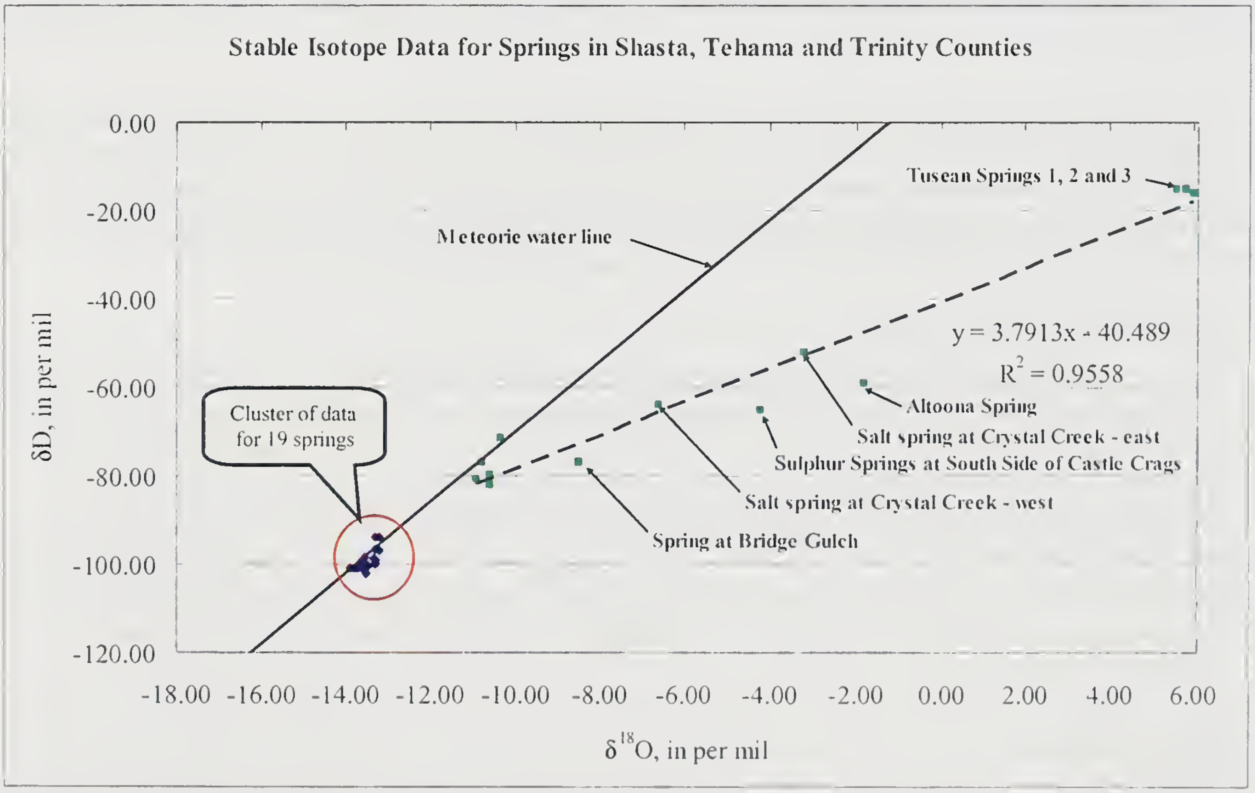

Figure 9. Barnes and Mariner stable isotope data for Shasta, Tehama, and Trinity Counties.

One obvious observation regarding this graph is the cluster of data (19 springs) that plot essentially on the meteoric water line in the vicinity of $\delta^{18}O$ of 13.5 and δD of 100. Most ocean water has a $\delta^{18}O$ value of 0 ± 1 and a δD value of 0 ± 5 per mil relative to SMOW (Craig and

Gordon, 1965). The meteoric water line in the graph represents water that falls as precipitation, with the distance away from zero along the line reflecting the conditions (latitude, elevation, etc.) under which the rain fell. The fact that a second group of data plot at different locations and predominantly away from the meteoric water line reflects a different set of conditions that has affected the composition of those waters. The data that plot significantly to the right of the meteoric water line are isotopically heavier as compared with data associated with most other springs in the area. There are several possible explanations for this "oxygen shift" in the data. If a line is drawn through the points that exhibit the oxygen shift, the result is a line with a lower slope than the meteoric water line with the origin on the meteoric water line. The slope of this line is about 3.8 and this change could be explained by enrichment during secondary fractionation processes. The slopes of data for water undergoing evaporation are less than 8, and commonly between 4 and 7 (Kendall and McDonnell, 1998).

An alternative explanation for the oxygen shift is that the water may have been altered as a result of temperature-dependent water/rock isotope exchange reactions. The $\delta^{18}O$ contents of both crystalline and carbonate rocks are considerably higher than meteoric water. Even a minor isotopic exchange will cause a shift in the ratio. In most aquifers, the temperature is too low and circulation rates too high for any significant alteration in the isotopic composition of groundwater. However, in geothermal systems above about 100° C, the increased temperature will increase the rate of isotopic exchange. A $\delta^{18}O$ shift due to geothermal alteration reflects an evolution towards isotopic equilibrium between the host rock and the water.

Another possibility is that the springs produce connate water from an ancient time of deposition when ocean water had $\delta^{18}O$ concentrations different then ocean water today. This explanation would be consistent with a seawater source; however, it is doubtful since the original water would have been expelled from fine-grained sediments during the shale-forming process (presumably up to 330 million years if the Bragdon Formation is the source).

Ammonium Concentrations
Data in the Barnes and Mariner database suggests ammonium concentrations for the "West" and "East" springs of 21 and 19 mg/l, respectively. Such values are high given the location of the springs far from potential anthropogenic contaminant sources. However, if geothermal activity has played a role in the alteration of the water, that could potentially explain this. Only three other springs in the three-county area produced water with ammonium concentrations greater than 3 mg/l. Those springs were Altoona Spring, Spring at Bridge Gulch, and Sulphur Spring on south side of Castle Crag which produced 20, 26 and 29, respectively. However, this statistic is misleading, since the database only contains ammonium results for a total of 11 springs.

Discussion
James (1990) theorized that groundwater flowing through the Bragdon marine-deposited shales and sandstones dissolves salts before being impeded by faults and the nearly impervious Copley Greenstone. The report goes on to suggest that groundwater at depth finds a flow path within the Copley Greenstone fracture system, then flows back to the surface.

Scott Lewis (pers. comm.), a Caltrans geologist, proposed an alternative conceptual model of the groundwater flow system for Salt Springs at Crystal Creek. That theory has recharge water entering the Copely Greenstone southwest of the site and northeast of the Shasta Bally batholith, then moving down-gradient to the northeast past a heat source, where it encounters joints just prior to reaching the Spring Creek Thrust Fault. Although James (1990) does not discuss this second theory, he did note that Willow Creek's incision through fractured bedrock had not intercepted (cut off) mineralized water from occurring on the southwest side of Willow Creek. This observation would be consistent with Lewis' alternate conceptualization of flow.

The Piper trilinear plot (Figure 7) indicates that most of the data for springs in Shasta, Tehama and Trinity counties plot somewhat linearly. This suggests that water may have evolved along a similar flow path. The Salt Springs at Crystal Creek data, on the other hand, plot away from these trends and near the Puget Sound seawater data. This suggests not only differing chemistry between the water from Salt Springs at Crystal Creek and that from other springs, but also potential similarity between the water at the *P. howellii* springs and a source with mineralogy somehow linked to seawater.

The specific conductance versus chloride concentration graph (Figure 8) indicates that data for the Salt Springs at Crystal Creek plot along a different linear trend than most other springs. This suggests that they share a different relationship between these two parameters compared to most other springs in the three-county area.

The $\delta^{18}O$ and δD plot (Figure 9) indicates that a group of data, including those from the Salt Springs at Crystal Creek, plots predominantly below and to the right of the meteoric water line. One possible explanation for this oxygen shift is that the water underwent enrichment during a secondary fractionation processes (evaporation). A viable alternate explanation is that the oxygen shift is due to water-rock interactions, perhaps at an accelerated rate due to geothermal alteration.

It is significant that the isotopically heavier (oxygen shifted) data in Figure 9 plot quite linearly, with an R^2 coefficient of 0.96. This linearity may be indicative a common process that has affected all of these waters such as a common deep flow path or potentially similar types of geothermal alteration.

It must also be noted, however, that due to some irregularities with the Barnes and Mariner general chemistry data, there are concerns regarding the validity of the δ18O and δD results. For instance, the pH for the "West" and "East" springs are listed as 9.35 and 6.75, respectively, and the temperature results are listed as 19 and 30 degrees C, respectively. These differences could either indicate differing water at the two different springs or that there were problems with the sampling techniques. Further differences between the Barnes and Mariner and the Caltrans data may shed some light on this. For example, the $\delta^{18}O$ results for the "East" spring which are listed as -3.2% in the Barnes and Mariner database and -6.2, -6.15 and +1.4% for springs 2A, 2B and 3B, respectively, by Caltrans. This raises questions of where these samples were collected, how much they equilibrated with the atmosphere, whether there was degassing, and how the chemistry may have been altered after it reached the surface (possibly by subsurface mixing with meteoric water). This might not be as significant for the major dissolved constituent data, but would be significant regarding the stable isotopes.

Some details about Caltrans efforts to collect water temperature data demonstrate problems with the methods used to sample diffuse flow at the site. However, despite such difficulties, it should be noted that the 30 degrees C temperature for the "East" spring recorded in the Barnes and Mariner database is significantly warmer than any of the Caltrans data. If this is accurate, then that spring's temperature was high enough to indicate either a very deep flow path or geothermal conditions, at least when that sample was collected. As the water would be expected to cool down rather than heat up as it flowed over the surface, the value of 30°C is questionable.

Ammonium concentrations recorded in the Barnes and Mariner database may also provide evidence regarding potential geothermal alteration. Water from the "West" and "East" springs produced ammonium concentrations of 21 and 19 mg/l respectively. Such values are high given the locations of the springs far from any potential anthropogenic contaminant sources. However, if geothermal activity played a role in the alteration of the water, that may potentially explain such high concentrations. Hydrolysis of cyanide could be another source of the observed ammonium concentrations. Only three other springs in the three county area produced water with ammonium concentrations greater than 3 mg/l. Those springs were Altoona Spring, Spring at Bridge Gulch, and Sulphur Spring on south side of Castle Crag, which produced 20, 26 and 29, respectively. As these springs also were five (including the "East" and "West" springs) of the eight springs with oxygen shifted data on the $\delta^{18}O$ and δD plot, it is tempting to conclude that geothermal alteration was the cause. However, the Barnes and Mariner database only contains ammonium results for a total of 11 springs, thus this evidence is not conclusive.

There is limited information to go on with regard to discerning the source(s) of groundwater at the *P. howellii* spring site. Nonetheless, three potential scenarios were developed as conceptual models of groundwater flow to the springs. Figures 10, 11, and 12 present schematic cross sections depicting each of these scenarios. All three suggest that fracturing and jointing in the area has led to secondary permeability and that the potentiometric surface intersects a low point in the topography at the same point where a fault system supplies an open fracture pathway upward through the Copely Greenstone.

Scenario 1 in Figure 10 suggests that groundwater flowing through fractures in the Bragdon marine-deposited shales and sandstones dissolves salts before being impeded by the Spring Creek Thrust Fault and the nearly impervious Copley Greenstone. This scenario further suggests that the groundwater at depth finds a flow path within the Copley fracture system that allows the water to reach the surface in the vicinity of the springs. This is basically the theory presented by James (1990), which presents arguments for groundwater flow through the Bragdon Formation as a potential source of water at the springs. Additional evidence is contained in the Piper trilinear plot (Figure 7) which indicates a similarity between the chemistry of the spring water and Puget Sound seawater. However, while it is possible that the groundwater dissolves minerals as it percolates through the formation's marine rocks, there are no references to salt deposits associated with the Bragdon Formation. Furthermore, the Bragdon Formation lacks primary (intergranular) permeability, and secondary permeability exists only where this formation is fractured and jointed. Regarding a potential connate water explanation for the presence of saline waters emanating from the Bragdon Formation, this seems unlikely as the original water would have been expelled from the sediments long ago during the shale-forming process.

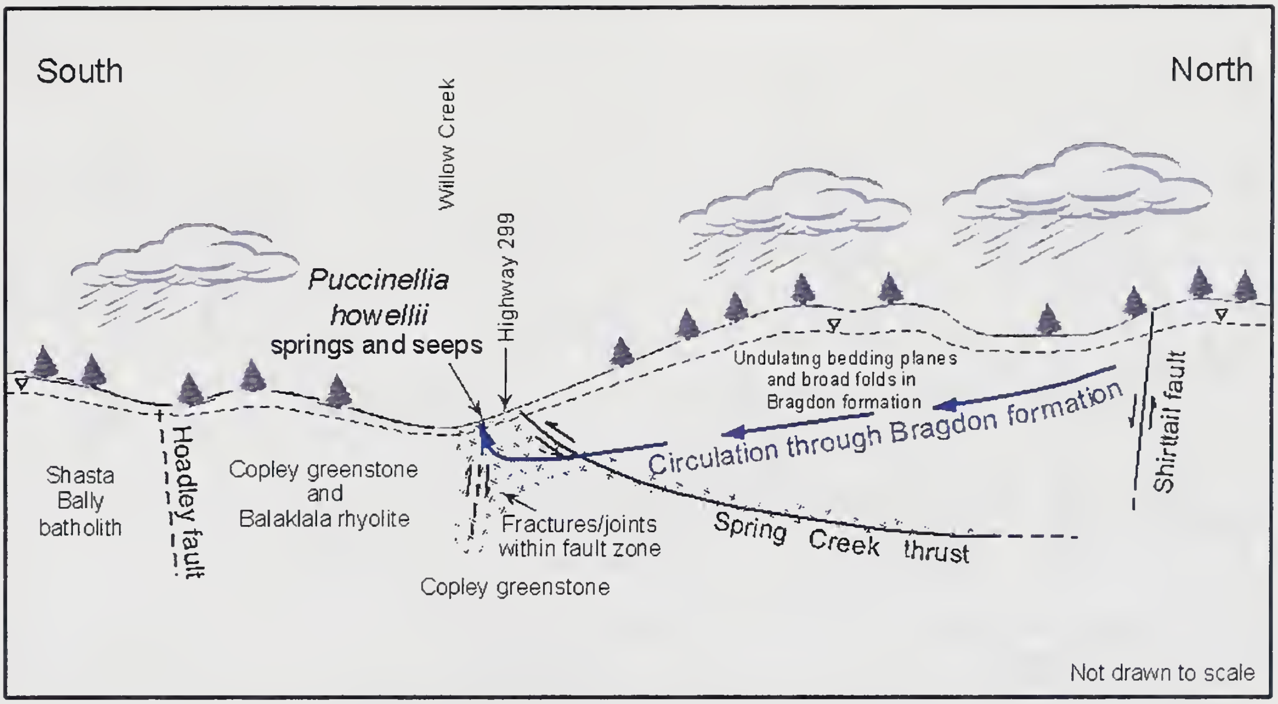

Figure 10. Scenario 1 of potential groundwater flow to the spring site.

Scenario 2 in Figure 11 depicts water discharging at the *P. howellii* springs as having experienced a deep circulation flow path through the Copely Greenstone. The portion of the figure suggesting that flow may come from the southwest is similar to what has been suggested by Lewis (pers. comm.). As for the potential of deep circulation water coming from the north, it is possible that the thrust fault may act as a fault-gouge confining unit, thus creating a regionally confined aquifer system. This system may have been breached by the high angle faults in the vicinity of the Salt Spring site, thus allowing water from the Copley Greenstone to rise to the surface. This theory of the potential movement of deep circulation water from the north or south along fault-related fracture zones has also been suggested by Penoyer and Martin (2007).

Some evidence supporting the Figure 11 hypothesis includes a borehole completed south of the Spring Creek Thrust Fault within the Copely Formation that produced water at a depth that was only slightly mineralized (Caltrans, 1991). This suggests the saline water is derived from a deep source. Also, James (1990) indicates that mineralized water occurred on the southwest side of Willow Creek, at least at that time. In contrast to this supporting evidence, one typically would not expect water traveling through rocks associated with the Copely Greenstone or the Shasta Bally batholith to pick up such high percentages of either Cl of SO_4 - even with a long flow path and long residence times. Consequently, some sort of geothermal alteration would be required. The Shasta Bally batholith theoretically could have provided a heat source for such alteration. As such, it is possible that a reservoir of hydrothermally altered water, now cooled, could exist and is being slowly released along the high angle faults. However, the Jurassic or Cretaceous age of the Shasta Bally batholith makes this theory appear a bit of a stretch. Consequently, the Scenario 2 explanation in conjunction with a more recent heating event would seem more likely.

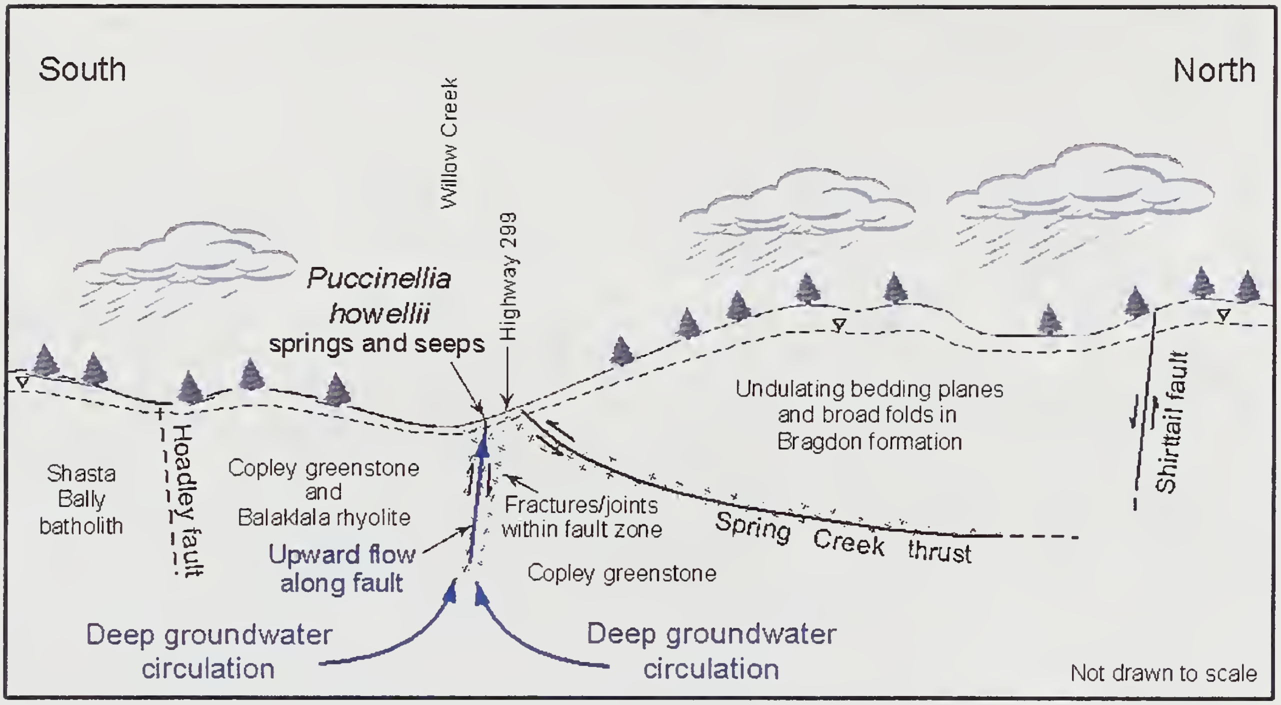

Figure 11. Scenario 2 of potential groundwater flow to the spring site.

Scenario 3 in Figure 12 depicts water emerging at the site as initially having followed the path of secondary permeability created throughout a large portion of the Spring Creek Thrust Fault. If this is the case, then this water may emerge at the *P. howellii* springs site simply as a continuation along this fracture path – aided in reaching the springs by local fracturing associated with several high angle faults. Support for this theory includes those same arguments in favor of the conceptualized cross section depicted in Scenario 1, and the fact that this would explain the secondary permeability in the Bragdon Formation. If this hypothesis is correct, however, then one might expect to see more saline seeps along the extent of the entire thrust plane contact, and particularly along the lower hillsides. Instead, we only find these seeps/springs at a location where two high angle faults have intersected the Spring Creek Thrust Fault in conjunction with the topographic low of Willow Creek.

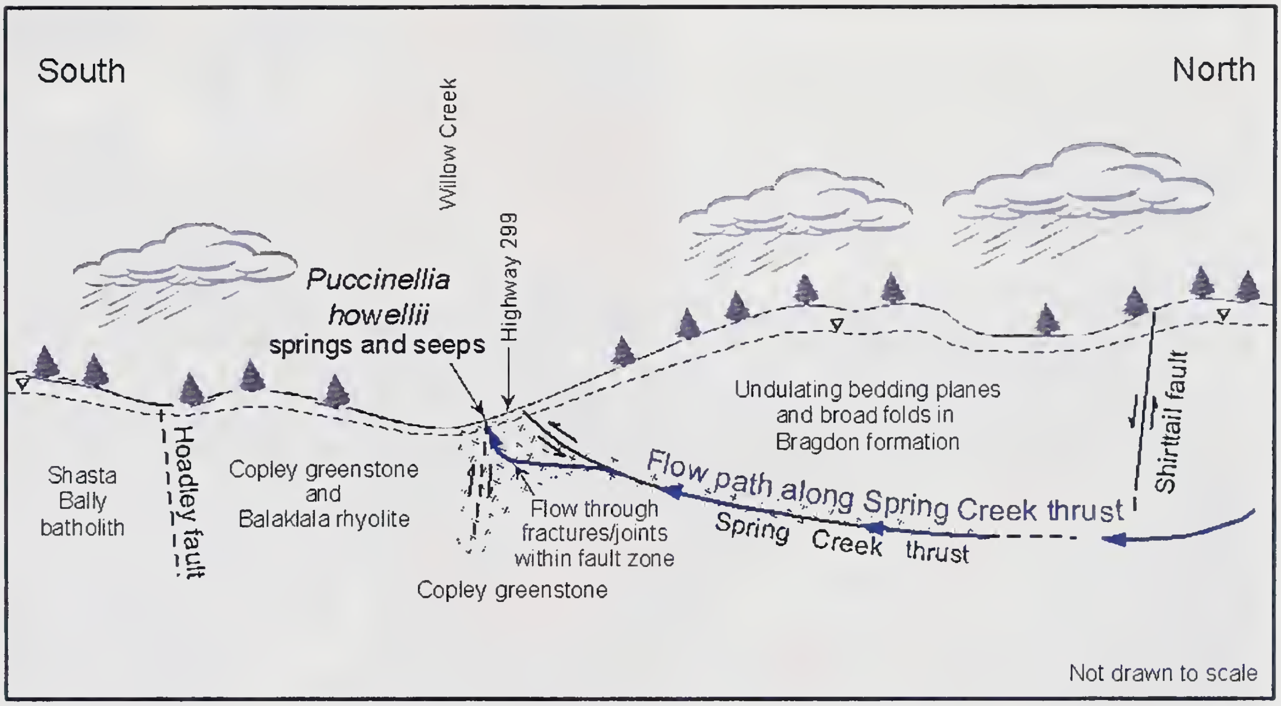

Figure 12. Scenario 3 of potential groundwater flow to the spring site.

Additional clues as to the source(s) of saline water to the springs may be found in the similar chemical characteristics of water from the Salt Springs at Crystal Creek and other springs found in the three-county area. These other springs include:

a) Spring at Bridge Gulch and Hunt Hot Spring, which plotted somewhat similarly on the Piper trilinear diagram;
b) Spring at Bridge Gulch and Spring in vein of magadiite, which plotted somewhat similarly on the specific conductance versus chloride concentration graph;
c) and Altoona Spring, Spring at Bridge Gulch, Sulphur Spring on south side of Castle Crag, and Tuscan springs #1, #2 and #3, which all plotted significantly to the right of the meteoric water line on the stable isotope data plot.

Of these, water from Spring at Bridge Gulch is the most similar to water from Salt Springs at Crystal Creek, as indicated on all three plots.

In order to help evaluate potential lithologic reasons for the somewhat similar chemistry, locations of all eight of these springs were plotted on a generalized geologic map (Figure 13). This map suggests that springs that produced water with somewhat similar chemical characteristics emerge from a variety of rock types. The Bridge Gulch site is located on terrain composed of gneiss and amphibolite derived from Copely, Balaklala, and Bragdon Formations. Additionally, the Spring at Bridge Gulch site is flanked by outcrops of the Bragdon Formation several miles to the north and Copely Greenstone several miles to south. The proximity to these two types of rock that are also found at the *P. howellii* springs site may be more than a coincidence.

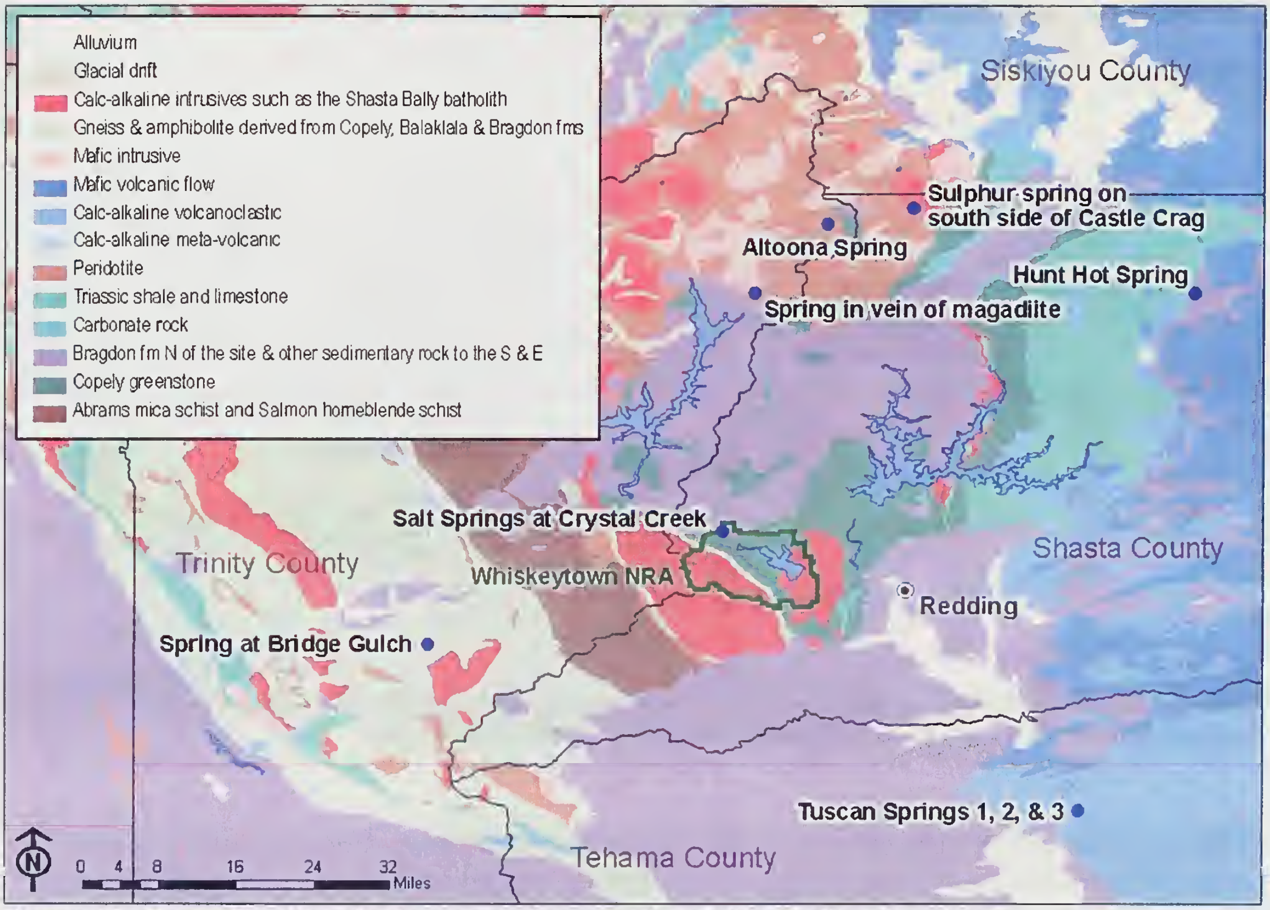

Figure 13. Generalized geologic map and area springs with similar chemistry.

Based on the information above the "Spring at Bridge Gulch site" appears to be the strongest candidate for establishing new populations of *P. howellii*, since the water chemistry is similar to that of the Salt Springs at Crystal Creek (Table 6). It is also interesting to note that previously Caltrans searched a number of other mineralized springs in northern California for additional sites that might support *P. howellii*. Out of the14 sites Caltrans evaluated, only three had data in the Barnes and Mariner database and thus were included as a part of this investigation (not counting the Salt Springs at Crystal Creek themselves). Of those three, only one plotted similar to the Salt Springs at Crystal Creek data on any of the three plots. That one site is Tuscan Springs, which is located about 50 miles SE of the site near Redding. Unfortunately, none of the other springs visited by Caltrans, including the Tuscan Springs site, apparently possessed habitat that was conducive for populations of *P. howellii.*

Table 6. Water chemistry at several candidate sites for introduction of *P. howellii.*

Name	Lat.	Long.	Date	T°C	pH field	Sp. Cond (mS)		δD	$\delta^{18}O$
Altoona Spring	41.138	-122.486	7/27/79	13	6.68	13,100		-59	-1.8
Hunt Hot Spring	41.033	-121.931	8/21/73	58	8.8	1,630		-94	-13.3
Salt Spring at Crystal Creek - West	40.668	-122.648	7/24/79	19	9.35	15,900		-64	-6.6
Salt Spring at Crystal Creek-East	40.668	-122.515	7/24/79	30	6.75	26,700		-52	-3.2
Spring at Bridge Gulch	40.495	-123.102	7/26/79	13	7.25	22,600		-77	-8.5
Sulphur Spring on south side of Castle Crag	41.162	-122.359	7/28/79	12	10.16	13,100		-65	-4.2

Name	Ca	Mg	Na	K	Alk.	NH_4	Cl	F	SO_4	SiO_2
Altoona Spring	51	210	3,600	290	8,310	20	1,300	4	460	79
Hunt Hot Spring	52	<0.1	300	4.3	62		140	3.6	520	47
Salt Spring at Crystal Creek - West	1,150	0.25	2,650	7.7	52	21	6,100	<0.5	<1	15
Salt Spring at Crystal Creek-East	2,000	0.56	5,000	16	~10	19	11,100	<0.5	<1	21
Spring at Bridge Gulch	1,000	285	4,150	24	114	26	9,200	<0.5	<1	12
Sulphur Spring on south side of Castle Crag	1	2.5	3,550	125	4,850	29	2,650	7.2	360	20

Conclusions

Based on the results of the geochemical analyses and the existing geologic and hydrogeologic information, three scenarios were developed regarding potential sources of groundwater to the *P. howellii* springs.

Scenario 1 suggests that groundwater flowing through the Bragdon marine-deposited shales and sandstones dissolves salts before being impeded by the Spring Creek Thrust Fault and the nearly impervious Copley Greenstone. This scenario further suggests that the meteoric groundwater flowing along the thrust fault at the base of the Bragdon Formation finds a flow path into the Copley Greenstone high-angle fracture system and then to the surface. Based on the results of this investigation, Scenario 1 appears to be the least probable conceptual model. Although it is possible that the groundwater dissolves minerals as it percolates through these marine rocks, there are no references to evaporite deposits or other sources of chloride associated with the Bragdon Formation. Additionally, in the absence of fracturing and jointing, these rocks have very low permeability.

Scenario 2 suggests that water discharging at the Salt Springs at Crystal Creek has experienced a deep circulation flow path through the Copely Greenstone. This scenario includes the possibility that the thrust fault is acting as a fault-gouge confining unit, creating a regionally confined aquifer system that has been breached by Willow Creek and the high angle faults in the vicinity of the site. This appears the most likely explanation for the saline groundwater that emerges at the *P. howellii* springs site. However, due to the mineralogy associated with the Copely Greenstone and the Shasta Bally batholith, this scenario would also likely need to include a component of geothermal alteration. As the age of the Shasta Bally batholith makes it an unlikely heat-source candidate, some unknown more recent heat source would seem likely.

Several aspects of other geochemical results of this study point to Scenario 2 as the most plausible explanation. For example, the oxygen shift in the subject spring data on the $\delta^{18}O$ and δD plot may indicate geothermal alteration of groundwater. Also, the oxygen shifted data in Figure 9 plot quite linearly, with an R squared coefficient of 0.96. This linearity may be indicative a common process that has affected all of these waters and that could relate to a common deep flow path or potentially similar types of geothermal alteration. Additionally, if the 30 degrees C temperature for the “East” spring is accurate, that is high enough to indicate either a very deep flow path or geothermal conditions when that sample was collected. Water from the “West” and “East” springs had ammonium concentrations of 21 and 19 mg/l respectively. Such values are high for springs that are located far from any potential anthropogenic contaminant sources. Geothermal activity could explain these high concentrations of ammonium. Hydrolysis of cyanide could be another source of the observed ammonium concentrations.

Scenario 3 suggests that water emerging at the site initially has followed a path of secondary permeability created throughout a large portion of the Spring Creek Thrust Fault. If this is the case, then this water may emerge at the subject site as a continuation along this path, also aided by fracturing associated with several high angle faults. This theory is supported by those same arguments made in favor of Scenario 1 and also would explain any regionally extensive secondary permeability along the thrust fault at the base of the Bragdon Formation. Consequently, this cannot be ruled out as a plausible explanation for the saline groundwater that emerges at the *P. howellii* springs site.

If groundwater flow characterized by long residence times and deep circulation through fractured Copley Greenstone depicted in Scenario 2 is the correct paradigm, then that would likely indicate the springs are not very susceptible to effects from anthropogenic development surrounding the park. However, the moderately deep flow path depicted in Scenario 3 would not likely include equally long residence times and equally deep circulation. As such, if Scenario 3 is correct, this would suggest that groundwater discharging to the Salt Springs at Crystal Creek would be most susceptible to the effects of anthropogenic development near the margins of the Spring Creek Thrust Fault block.

Perhaps the most significant conclusion to be made from this investigation is that the water discharging at Salt Springs at Crystal Creek is very unique. Only one other spring in the three-county area, the Spring at Bridge Gulch, produced somewhat similar chemistry on all three plots. If researchers were to attempt establishment of *P. howellii* at another site, it would seem that this location might make an interesting candidate. However, given the limited tolerance of this rare

salt grass for unsuitable habitat, it seems rather unlikely that it could exist at many other places in the world.

Recommendations for Future Work

The scope of this investigation was limited, and many questions remain regarding the source of saline groundwater at the *P. howellii* springs site. As noted, there are concerns regarding the validity of some of the Barnes and Mariner data, particularly the recorded values for temperature and pH and the implications this may hold for $\delta^{18}O$ and δD. As a result, repeating much of the previous sampling and analyses would help address the validity of the data. The parameters repeated should include all those discussed in this report, including the major dissolved constituents, stable isotopes, and some compounds such as ammonium. Temperature should be measured at the spring orifice. The samples should be collected as close to the spring orifice as possible and perhaps in very shallow (one meter or less) piezometers installed using a hand auger. Also, it may be useful to resample some of the monitoring wells previously installed by Caltrans, as well as the springs noted by Caltrans existing on the south side of Willow Creek. If temperatures are again measured, this need not be done continuously; rather, it is important that the measurements be made before the samples have a chance to equilibrate with the air.

There are a number of other geochemical techniques that have not previously been used at the site that could be helpful. For example, the trace elements boron, iodide, and bromide have been used elsewhere to help determine the origin of groundwater in coastal areas where seawater, high-chloride water from partly consolidated marine deposits, and irrigation-return water may contribute to high chloride concentrations in wells (Piper and Garrett, and others, 1953). Additionally, plots of the ratio of chloride to boron, iodide, and bromide as a function of chloride have been helpful to determine the relation of high-chloride waters from various sources (Izbicki, 1991, 1996).

More detailed mapping of the geology, including the faults, joints and fractures in the vicinity of the springs, could add greatly to the understanding of the hydrogeology of the site. In particular, greater understanding of the faults would be useful, as observations by Penoyer and Martin (2007) suggest that Albers may have incorrectly located at least one of these, and as a result, their role as either conduits or barriers is poorly understood. More detailed geologic mapping would more accurately locate faults in the area relative to the springs, allowing better interpretation of the role of fractured rock associated with the fault zones on groundwater flow paths to the springs.

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